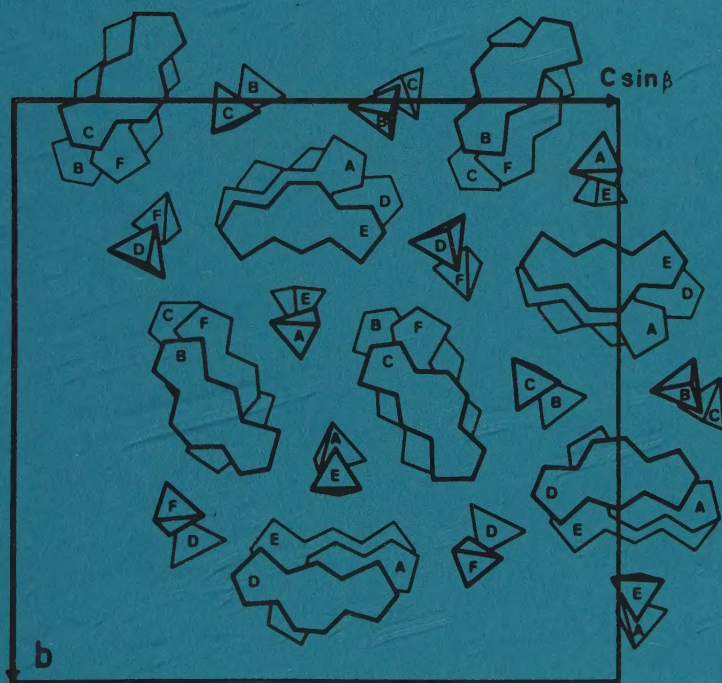


CRYSTALLOGRAPHIC AND CHEMICAL STUDIES ON SOME CYCLOHEPTADITHIOPHENE COMPOUNDS

Crystal and Molecular Structure in Relation to
Chemical and Physical Properties

Jan-Erik Andersson



Lund 1981

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Chemical and Physical Properties

BY

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Title and subtitle CRYSTALLOGRAPHIC AND CHEMICAL STUDIES ON SOME CYCLOHEPTADITHIOPHENE COMPOUNDS Crystal and Molecular Structure in Relation to Chemical and Physical Properties		
Abstract The crystal structures of a series of <u>cycloheptadithiophen-ones</u> and <u>cycloheptadithiophenylum perchlorates</u> have been determined at <u>low temperature</u>. The latter ones are <u>layer or columnar structures</u>. A <u>metastable</u> modification and the corresponding stable one exist. There is <u>disorder</u> of anions and for the metastable phase also of cations. The disorder has been studied. The anions in layers or columns can readily be <u>exchanged</u>. <u>Refractive indices</u> have been studied and related to structure. The <u>charge distribution</u> in the cation probably influence coordination of anions. The molecules are roughly <u>planar</u> due to delocalized electron systems, with a minor bend of molecules due to <u>angular strain</u> and <u>intramolecular interactions</u>. Alternation of bond lengths indicate <u>conjugation</u> in agreement with chemical and spectroscopic data.		
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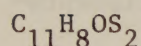
CONTENTS

1	INTRODUCTION	page 5
2	EXPERIMENTAL	11
	2.1 Preparative Work	11
	2.2 Substitution with Other Anions	14
	2.3 Phase Investigations	20
	2.4 Morphology	23
	2.5 Optical Properties	26
	2.6 X-ray Diffraction Work	34
	2.7 Determination and Refinement of the Structures	38
3	CRYSTAL STRUCTURE	43
	3.1 Description of the Structures	43
	3.2 Short Contacts Between Molecules or Ions	49
	3.3 Coordination	56
	3.4 Disorder	64
4	MOLECULAR STRUCTURE	71
5	SUMMARY	91
6	ACKNOWLEDGEMENTS	93
7	REFERENCES	94

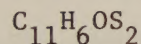
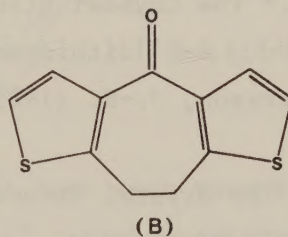
1. INTRODUCTION

The crystal structure of some compounds, with building units of great similarity, have been determined. By the knowledge of the crystal structure, it has been possible to describe, not only the way molecules are stacked together to form a crystal, but also their configuration. The mode of packing of the constituent units largely contributes to the physical properties of a crystal, and the configuration of molecules have connection with their chemical properties. Therefore, also knowledge of physical and chemical properties has been used in order to establish relations between structure and properties.

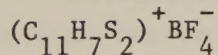
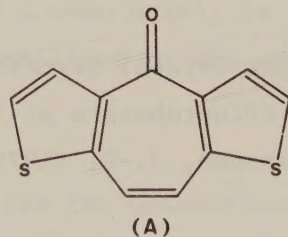
The compounds, which have been studied, are given with formula, notation and name in the following.



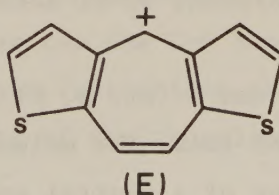
8,9-dihydro-4*H*-cyclohepta-
[1,2-*b*:5,4-*b'*]dithiophen-4-one

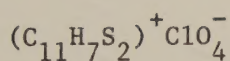


4*H*-cyclohepta[1,2-*b*:5,4-*b'*]-
dithiophen-4-one



dithieno[1,2-*b*:5,4-*b'*]tropylium
tetrafluoroborate

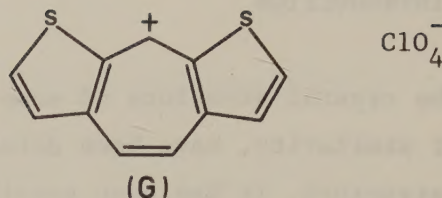




dithieno[2,1-*b*:4,5-*b'*]-
tropylium perchlorate

or

9*H*-cyclohepta[2,1-*b*:4,5-*b'*]-
dithiophen-4-ylum perchlorate



The structures of the above compounds have been published in Acta Crystallographica, under the heading of X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems. They are:

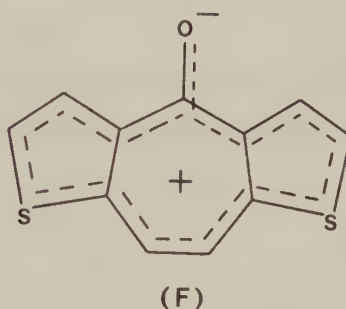
Compound	Article
B	III.* The Crystal Structure of 8,9-Dihydro-4 <i>H</i> -cyclohepta[1,2- <i>b</i> :5,4- <i>b'</i>]dithiophene-4-one Andersson, J.-E. (1975) Acta Cryst. B31, 1396-1399.
A	V.* The Crystal Structure of 4 <i>H</i> -Cyclohepta[1,2- <i>b</i> :5,4- <i>b'</i>]-dithiophen-4-one Andersson, J.-E. (1978) Acta Cryst. B34, 2235-2241.
E	X. The Crystal Structure of Dithieno[1,2- <i>b</i> :5,4- <i>b'</i>]tropylium Tetrafluoroborate at 143 and 295 K Andersson, J.-E. (1979) Acta Cryst. B35, 1349-1354.
G II	XI. The Crystal Structure of 9 <i>H</i> -cyclohepta[2,1- <i>b</i> :4,5- <i>b'</i>]-dithiophen-4-ylum Perchlorate at 173 K Andersson, J.-E. Acta Cryst. Accepted for publication.

Compounds A and B (cf. p. 5) are built up of molecules, whereas E and G consist of ions. The molecules (or cations) are cyclic ring systems, consisting of a central seven-membered ring and annelated thiophene rings. There are alternating double and single bonds, i. e. a system of conjugated double bonds.

The ring systems of the compounds can be thought of as a series. They are very similar but the bonding situation differ. Thus B is a

cycloheptadienone, A is a cycloheptatrienone and E and G are cycloheptatrienylium ions.

The ring systems have conjugated double bonds, which open the possibility of stabilization through π -electron delocalization. Resonance structures can be written for E and G, implying extensive conjugation and aromatic properties. Here, it is necessary to assume that the molecule is planar, to give a large overlap between π -orbitals. An extensive conjugation and strong polarization of the carbonyl group in the cycloheptadithiophene-ones is possible as shown by formula (F).



Chemical and spectroscopic methods have been used by Baruch Yom-Tov (1972) to study aromatic properties of cycloheptadithiophenes. The results were the following. The tropylium ions E, G were found to be relatively stable to hydrolysis (and G even more), in accordance with the assumption of a planar system stabilized by the effect of extensive conjugation.

The polarization mentioned above for the unsaturated cycloheptadithiophene-one A, was indicated by some chemical reactions and could be shown spectroscopically. The C-O stretching frequency (IR) is much lower for the unsaturated compound A than for the saturated B and this suggests a high degree of single bond character for the C-O bond in A, which means a highly polarized carbonyl bond. These indications of a semiaromatic system A also suggest a high stability of the tropylium ion E.

The fine structures in UV also indicate aromatic character. By NMR the thiophene protons were found to give a downfield shift on insertion of a double bond in the cyclohepta-dithiophene-one B. Thus, the above results found by Yom-Tov are in accordance with the assumptions of planar conjugated systems. However, it could not be shown definitely whether

the molecules really are planar, or not. From the chemical and spectroscopic evidence mentioned above it is concluded that the compounds B, A, E form a series of molecules of increasing aromaticity. G is even more aromatic than E.

The present work began with the intention to study the conformations of cyclic compounds of the type discussed above. As exemplified above, the chemical properties of a compound are dependent on the configuration of the molecules. With X-ray crystallographic methods, the configuration of a molecule in the crystalline state can be revealed in great detail, and used for drawing conclusions on chemical properties. E. g. distances between atoms can be used to study the extent of conjugation and angles to estimate angular strain. In the present series of decreasing aromatic properties, an analogue alteration in geometry of the molecules would be expected.

Not only the configuration of molecules, but also the whole arrangement in the crystals is revealed. B and A are molecular compounds, while E and G are ionic compounds, and especially the latter crystals have presented problems of crystallographic nature, which have actualized studies also of their physical properties. Problems, such as how the large ions are packed most efficiently, how the large cation is coordinated by anions and disorder of anions have been studied. The arrangement of molecules in crystals largely determine their morphology and their optical properties i. e. refractive indices in different directions. Other properties which are related to the packing of molecules are ionic mobility and stability relations. Thus, knowledge of the crystal structure of a compound can be used to draw conclusions about various physical and chemical properties of crystals.

The description of the work by the author begins with the preparative work, which includes recrystallizations and preparation of polymorphs. Some experiments to exchange the perchlorate ions to other ions were made in order to study the effect of this on the crystal structures. Stability relations between different phases were also studied. In connection with the investigations of structures of different phases some physical properties were measured in order to correlate these to the structures.

In X-ray Diffraction Work the measurements on a single crystal are described, and in Determination and Refinement of the Structures the calculations on these data is taken up. In Crystal Structure the results of the structure determination are used for showing how molecules build up the crystal, and comparisons between structures are made.

In Molecular Structure the conformations of the molecules are discussed and compared between different compounds. From the conformations various conclusions are drawn e. g. about conjugation, angular strain and intramolecular H-H interactions. The chemical properties are compared with these results.

After this follow a summary, acknowledgements and references. This work will be a description of structures and also an attempt to use the information of geometric nature about structures to correlate it with physical and chemical properties.

EXPERIMENTAL

2. EXPERIMENTAL

2.1 Preparative Work

Syntheses. All the compounds were synthesized by Baruch Yom-Tov (Diss. 1972). He recrystallized them by saturating a boiling acetonitrile-solution with a compound, and then allowing the solution to cool down in air (or in a refrigerator). From such batches, single crystals for the X-ray work were picked out, though with some difficulty for some of the crystals. The author started experiments to recrystallize the compounds, in order to make it easier to obtain large single crystals. When trying to get G I, it was found that another phase (G II) was formed. This was the beginning of experiments with recrystallizations to get good crystals and to investigate the existence of polymorphs. Some data for the compounds are given in Table 2.1.

Recrystallization. The recrystallizations were performed, in the same way as by Baruch Yom-Tov, by cooling a saturated solution. The solution was filtered and then saturated by boiling off part of the solvent. The temperature of the boiling saturated solution was 90-95 °C, and the round flask containing it was put into a Dewar vessel with water of about 70 °C (Fig. 2.1). Thereby, the solution cooled down slowly to room temperature (about 24 hours). It was thought that the proper conditions for getting large crystals would be a slow cooling rate (Dewar vessel) and a clean-filtered (membran filter) solution. The crystals formed were washed first with $\text{CH}_3\text{CN-EtOAc}$ and then with EtOAc or ether.

E. When crystallizing E, some crystals were found when the Dewar vessel was opened at 25 °C. The crystals were discarded and the mother-liquor was allowed to cool down further in a refrigerator. More crystals were formed and among these some good ones were found.

G. When it was attempted to recrystallize the characteristic plate-like crystals of G, it was observed that instead needles were formed. At this time only a very limited amount of substance was available, so recrystallizations had to be performed on a rather small scale. It was found that the needles are another phase (G II) of G, with a large unit-cell (cf. Phase Investigations and Crystal Structure, Table 3.1). Later,

more substance was synthesized by Baruch Yom-Tov. Extended experiments were done to elucidate the conditions for the two phases to form. Now, using the procedure described, it was found that in general phase G I is formed. Only in one occasion G II was obtained. There is no explanation for this. *The safest method to get phase G II, is to rapidly cool the solution down in ice water.* Cooling in air gives G I. However, the faster cooling the smaller crystals. The product contains needles and among these some plates. Nucleation seems easy for G II and more difficult for G I, but once formed the crystals of G I grow faster. *This is in agreement with the fact that G II is metastable (cf. Phase Investigations), which implies a greater solubility.* It was tried to nucleate a solution with powder of G II, but no effect of this was observed. It should be pointed out that G I a few times have been obtained as flat needles, although generally as plates.

Various other attempts to crystallize G II were made. They were the following: Crystallization in different temperature intervals, very fast cooling (acetone - CO_2), evaporation at room temperature (CH_3CN or CHCl_3 - CHBr_3), precipitation from a solution in CH_3CN with EtOAc (G is only slightly soluble in EtOAc) and crystallization with other solvents. Mostly phase G I was formed, but at some occasions also phase G II. These methods had no advantage over the one given earlier.

Characterization. The different preparations were characterized by powder photograms recorded by a Guinier-Hägg focusing camera. By this method phases and quality of crystals can be evaluated. For cell dimensions cf. Crystal Structure, Table 3.1.

Table 2.1 Properties of the compounds.

Compound	Properties of crystals			Solubility in		Recrystallizations	
	Colour	mp °C	Form	CH ₃ CN	EtOAc	Solvent used	Not stable in
B	colourless	95	needle	good	some	CH ₃ CN	
A	yellow (faint)	172-3	plate rect.	good	some	CH ₃ CN	
E.BF ₄ ⁻	yellow-brown	310	plate	good	low	CH ₃ CN	H ₂ O
G I.ClO ₄ ⁻	yellow-brown	288	plate	good	low	CH ₃ CN	H ₂ O
G II.ClO ₄ ⁻	yellow-brown	288	needle flat	good	low	CH ₃ CN	H ₂ O

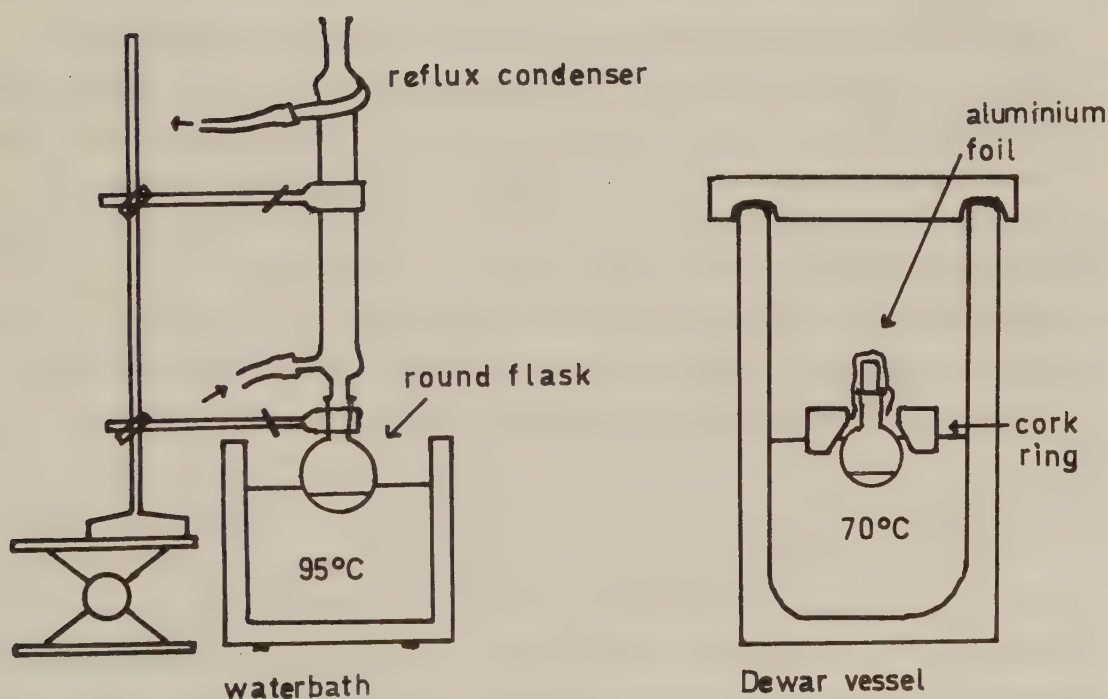


Fig. 2.1 The arrangements used for performing recrystallizations.

2.2 Substitution with Other Anions

When the structures of E.BF_4^- and G II.ClO_4^- had been solved, it was found that the anions were disordered (cf. Crystal Structure). Also in G I.ClO_4^- there is disorder of anions (Aurivillius, 1974). Moreover, the structures of E.BF_4^- and G I.ClO_4^- can be described as layer structures, where layers of cations are interleaved with layers of anions. In G II.ClO_4^- there are columns of cations with columns of ClO_4^- in between. It was therefore thought that, in the structures mentioned above, it would be possible to exchange the anions with other anions of about the same radius (e. g. I^-). Furthermore, these anions might arrange themselves in a more ordered way in the crystals, giving the possibility of a more refined structure determination. To give an apprehension of which anions might be used, some experiments under the microscope were performed. Compound G was used for the mainpart of the investigations, as it was available in a fair amount.

Precipitation. In the first experiment, a drop of a CH_3CN -solution of G.ClO_4^- was placed on an object glass (treated with silicon oil to prevent the drop from flowing out). A crystal, e. g. KI, containing the anion tried, was pushed into the drop. In some cases a rapid reaction occurred, see Table 2.2. From the KI crystal long red needles grew out rapidly. The needles showed extinction with polarized light. Very similar results were obtained with a KSCN-crystal. KBr gave a slow growth of irregular brown crystals. *These results indicate that the compounds with I^- , SCN^- and possibly Br^- have a low solubility. Thus, stable compounds are formed with these anions.*

Exchange. In the next experiment crystals of a compound, e. g. G I.ClO_4^- , were placed on an object glass, and a CH_3CN -solution of a salt e. g. KI, was added (Table 2.3). G I is attacked slowly by KI-solution, the attack preferably starting in cracks. In contrast, the attack on G II is fast, mostly starting at one end of a needle and rapidly progressing along the needle. The colour changes from yellow to bright red (Table 2.3). The behaviour is similar with KSCN. It seems as if the packing of ions in the needles of G II allows diffusion of I^- along the needles. This is in accordance with the structure of G II (cf. Crystal Structure, Fig. 3.5). In it there are columns of ClO_4^- -ions

in the direction of the a-axis. This direction is also the lengthwise direction of a needle (cf. Morphology).

A simultaneous transformation beginning at both ends of a needle was never observed. In the crystals of G I such a direction of transformation, as the one mentioned above for G II, was not observed (although still possible). The structure of G I shows planes of ClO_4^- -ions rather than columns (cf. Crystal Structure, Fig. 3.4). *The observations mentioned above indicate a large mobility of anions in the structure of G II and a somewhat lower one in G I.* In polarized light the red needles formed from G II did not show any extinction, in contrast to the yellow needles before attack. The absence of extinction with polarized light indicates that the crystal has turned polycrystalline. *The structure formed from G II with I^- -ions probably has cell dimensions and packing different enough to break the crystal during growth. Clearly, these reactions can be used for identification of phases and also give some information of the structure.*

Preparation. The crystals formed under the microscope were small, and it was tried to get large and good ones (to identify the phases) in the following way. $\text{G I} \cdot \text{ClO}_4^-$ was pulverized. The yellow powder and crystals of KI were shaken in CH_3CN . In a short time the colour of G turned red, and the mixture was allowed to stand for an hour. The red product was separated from the liquid. By the aid of a polarizing microscope crystals of KI and KClO_4 could be identified after evaporating a drop. There were crystals of KI in the above mentioned product, and it was tried to pick them out. The red product was solved in CH_3CN with the intention to recrystallize it by cooling the warm solution, in the same way as described in Preparative Work. Brown leaves, denoted (BL), were obtained after cooling. The solution was concentrated and after cooling red leaves (RL) were obtained this time. After leaving the remaining solution for some time (at room temperature), red crystals (RC), of a shape similar to G I, precipitated. KI-crystals were added to the solution and red crystals (RCR) (probably (RC) of another shape) immediately began to grow on them.

Identification. All the compounds prepared were not fully identified. The brown leaves (BL) are probably not an ionic compound (probably an ether), and the red leaves (RL) are probably $\text{G} \cdot 1/2 \text{ClO}_4^- \cdot 1/2 \text{I}^-$ (Table

2.4). The red crystals (RC) have the characteristic shape of $G I.ClO_4^-$ and probably the formula $G I.I^-$. Powder and Weissenberg photographs showed that $G I.I^-$ is isomorphous with $G I.ClO_4^-$.

The red crystals of another shape (RCR) are the same phase as (RC). This was indicated by Weissenberg recordings on one single crystal. Powder photographs and cell dimensions are given in Table 2.5 and 2.6.

Conclusion. It is concluded that there are crystals of G, with ions of similar size as ClO_4^- , e. g. I^- and SCN^- . The anions in $G I.ClO_4^-$ and $G II.ClO_4^-$ are easily exchanged to or substituted with I^- , indicating mobility of anions. There is not a gradual exchange of ions, however. One phase, probably with the formula $G I.I^-$, is isomorphous with $G I.ClO_4^-$.

Table 2.2 A crystal added to a drop of CH_3CN -solution of $G.ClO_4^-$.

Crystal added	Reaction	Reaction rate	Crystals formed colour shape		Extinction of product
KI	yes	fast	red (dark)	needles	yes
KSCN	yes	fast	red	needles	yes
KBr	yes	slow	brown	irreg.	-
$NaBF_4$	no				
KCl	no				

Table 2.3 A drop of CH_3CN -solution of a substance added to crystals of G.ClO_4^- .

Crystals of	CH_3CN -solution of	Reaction	Reaction rate	Way of attack	Extinction of product	Solubility of salt
G I. ClO_4^-	KI	yes	slow	starting in cracks	weak	some
	KSCN	yes	slow			good
G II. ClO_4^-	KI	yes	fast	starting at an end of a needle	no	some
	KSCN	yes	fast			good

Table 2.4 Some crystal data for the compounds obtained by substitution with I^- .

Notation	Colour	Shape	mp $^{\circ}\text{C}$	Density $\text{D}_m \text{ Mg m}^{-3}$	Cell volume $\text{\AA}^3$	Z	Vol per formula unit $\text{\AA}^3$
(BL)	brown	leaves	252	1.64	(965)		
(RL)	red	leaves	245	1.90	(2874)		
(RC)	red	plates	273	1.89	1151	4	288
(RCR)	red	bulky	273	1.90	1151	4	288

Notation	Formula	FW	Evaluated recordings	
			Powder	Wb
(BL)				x
(RL)	$\text{G I. } 1/2 \text{ClO}_4^- \cdot 1/2 \text{I}^-$			x
(RC)	$\text{G I. } \text{I}^-$	330.1	x	x
(RCR)	$\text{G I. } \text{I}^-$	330.1		x

Table 2.5 Measured and indexed lines of a powder photograph of G I.I^-

$\text{CuK}\alpha_1$ -radiation was used ($\lambda = 1.54051 \text{ \AA}$) and KCl was added as an internal standard ($a_{\text{KCl}} = 6.2930 \text{ \AA}$). For the lattice parameters cf. Table 2.6.

I_{obs}	$\underline{h}$	$\underline{k}$	$\underline{l}$	$10^5 \sin^2 \theta_{\text{obs}}$	$10^5 \sin^2 \theta_{\text{calc}}$	Comment
w	0	2	0	1612	1612	
w				1756		
st	0	2	2	2810	2812	
st	1	2	0	2921	2917	broad line
st	0	1	3	3083	3102	broad
w	1	2	1	3279	3279	
m	-1	0	3	3806	3819	
st	2	0	0	5215	5221	broad
w	1	3	1	5311	5294	
m	-1	2	3	5432	5431	
vw				5523		
m	1	3	2	6247	6256	
w				6498		broad
w	1	1	4	6776	6755	broad
w	1	4	1	8108	8115	broad
m	-1	0	5	8505	8494	broad
w	-2	3	2	9797	9800	
w	-2	3	4	13152	13151	

Table 2.6 Lattice parameters and systematically present reflexions.

Compound	Method and cell dimensions	Systematically present reflexions
(BL)	Weissenberg: rotation axis 12.805 Å a = 12.805 Å $\alpha = 90^\circ$ b = 9.58 c = 7.87 V = 965 Å ³	0k1: l = 2n 1k0: k = 0 3k0: k = 0
(RL)	Weissenberg: rotation axis 19.34 Å a = 24.48 Å b = 19.34 $\beta = 111.4^\circ$ c = 6.52 V = 2874 Å ³	
(RC) G I.I ⁻	Powder photogram: a = 6.75(2) Å $\alpha = 90^\circ$ b = 12.13(2) $\beta = 92.8(2)$ c = 14.08(1) $\gamma = 90$ V = 1151 Å ³	0k0: k = 2n h01: h + 1 = 2n Space group P2 ₁ /n

2.3 Phase Investigations

The phases obtained by recrystallizations and substitution with other anions were identified by powder and single crystal methods (cf. Preparative Work). The polymorphs of G were investigated in order to establish which polymorph is the stable one. It was tried to transform one into the other in two different ways, by temperature treatment and by treatment with the saturated solution.

Transformations, powder. Temperature treatment was tried first. The sample (G I och G II) was pulverized and heated to 185 °C overnight. It was checked by powder photograms if there was any change. Only when G II was used as starting material a change could be detected. It was transformed into G I in most of the experiments. *This indicates that G I is the stable polymorph at 185 °C, or that there is a transition point at this temperature.*

Single crystal. Experiments with single crystals of G II were also made. One isolated long single crystal of G II was divided in two parts. The first part was treated in the same way as above. No change occurred. This was checked by rotation photograms and a polarizing microscope. The other part was divided into three parts, separated from each other on an object glass. The first part was left as it was, the second part was kept in contact with powder of G II and the third one was left in contact with powder of G I. After heat treatment (175 °C, 8 days) it was found that the first part had not changed at all. The second part on the contrary, just showed a very weak extinction with polarized light and the third did not show extinction at all. Both gave powder lines in rotation photograms. The outer shape was unmodified. It was supposed that the latter parts had been transformed into G I and turned polycrystalline. *Evidently, there is a resistance to the phase transition, and a nucleation (or initiation of some kind) is needed to start the transformation.* The prepareate of G II, used for the powder to the second part of the crystal, did probably contain a minor part of the stable polymorph G I (cf. Preparative Work). The same transformation mechanism might be involved in the transformation of powdered G II to G I (see above).

Batch of single crystals. Also prepares of G II containing many small single crystals, and which were not worked mechanically (pulverized), were heat treated and inspected by the aid of a microscope. For some crystals the direction of extinction were unaltered in the lengthwise direction of them, but for the main part of them the extinction of the needles were not retained. Powder photograms indicated a certain proportion of G I after heat treatment, and thus part of the sample had gone through a phase transformation. However, one needle now had its direction of extinction at an angle of 27° to its length direction. Another larger needle had a part in the middle of it, which expelled the same phenomenon. *Thus, when a transformation was started the needles became polycrystalline or single crystals.* An explanation to this fact might be that when the transformation is initiated at one point (and if the crystal is of high quality), one single crystal can be obtained.

In the powder experiment on the contrary, the phase transition was easily obtained, possibly due to the mechanically worked sample containing very small crystals (probably also some crystals of G I). *Thus, the phase transition is probably initiated by nucleation or by mechanical treatment.*

The fact that a single crystal was obtained with an altered direction of extinction, indicate that there is a simple transformation mechanism between the structures of the metastable phase and the stable one.

Calorimetry. It was also tried to study the phase transformation by a calorimetric method (DSC, differential scanning calorimetry). A sample of G II was used. A phase transition of first order is accompanied by an evolution of heat, but this was not found anywhere between room temperature and the melting point. The reason why the phase transition was not observed is probably that the resistance to transformation is large. The sample did probably not transform or transformed so slowly that it was not detected. The sample was destroyed by melting and could not be investigated by powder methods. The scan time was 8° per minute. At some temperatures (169, 195-207, 231°C) there was a small absorption of heat, probably due to decomposition of the compound. It was namely observed earlier that the colour of the crystals slowly darken (from yellow-brown) at temperatures over 185°C , and decompose near the

melting point. Another possibility might be rotation of anions.

Solubility of phases. The other way to try to perform a phase transition was to shake crystals in a saturated solution of CH_3CN at room temperature for some days. It was originally attempted to measure the solubility of G II and G I, as the metastable phase should have a higher solubility than the stable one. The accuracy in the measurements was however not good enough as there probably is a very small difference in solubility. The crystals shaken were checked by powder photograms before and after shaking. The result was that G II had been transformed into G I in one experiment out of two. G I did not change. Thus, the phase transition also occurs at room temperature if the crystals of the metastable phase are in contact with the solution. The mechanism might be that G I grows at the expense of G II, or that the transformation of G II in the solid state is initiated.

Conclusion. It was concluded from the above results that G II is metastable and that G I is stable, at least from room temperature to 185°C .

Volume changes. The molar volume of $\text{G II} \cdot \text{ClO}_4^-$ is larger than that of $\text{G I} \cdot \text{ClO}_4^-$ (cf. Crystal Structure). This fact is in accordance with the conclusion above. It was not tried to perform the transformation by application of high pressure.

Iodides. Temperature treatment (180°C , 24 h) of pulverized samples of the iodide compounds resulted in decomposition. Crystals which were not pulverized, darkened but retained their extinction. The calorimetric method (DSC) used for $\text{G I} \cdot \text{I}^-$ indicated decomposition at 206°C (exotherm reaction). The temperature was probably unsuitably high for the purpose of studying phase transitions. It is likely that $\text{G I} \cdot \text{I}^-$, which is isomorphous with $\text{G I} \cdot \text{ClO}_4^-$, is the stable phase as it was easily obtained by crystallization. No corresponding compound to $\text{G II} \cdot \text{ClO}_4^-$ has been found.

2.4 Morphology

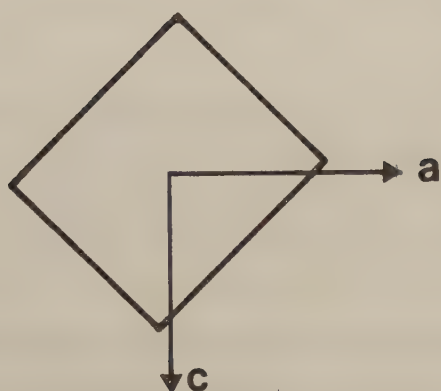
The present compounds have all relatively flat molecules. The ketones B and A form molecular crystals, held together by weak van der Waals bonds. E and G on the contrary, are ionic crystals with large molecular cations where also ionic forces will determine the packing.

Molecular crystals. Compound B forms needles elongated along the b-axis (Fig. 2.2). The result of the structure determination shows that the relatively flat molecules have their molecular planes approximately at right angles to the short b-axis (cf. Crystal Structure). It seems natural that when the crystal grows, the molecules pile up fastest in this direction and a needle is formed. The principal surfaces of crystals are those growing (thickening) slowly, having a large reticular density (Bunn, 1963). For B these are directed diagonally relative to the unit cell.

Ionic crystals. Crystals of E and G I are plates (Figs. 2.3 and 2.4). For E a needle-shaped crystal might be expected as all the cations are parallel (cf. Crystal Structure). The fact that plates are formed instead of needles, is probably an effect of ionic forces. The indices of the surfaces of E show that most surfaces correspond to the sides of the unit cell (Fig. 2.3).

G I has layers of cations. The cations are parallel within a layer. G I form plates at right angles to b (Fig. 2.4). The direction of growth seems different for these crystals compared to the other ones. It might be noted that both for E and G I needle shaped crystals have been observed at a few occasions.

G II on the contrary, are flat needles elongated along the a-axis, which is the direction of columns of cations (Fig. 2.5). The needles of G II are somewhat flattened, indicating a minor difference in rate of growth between the direction of b and c.



Pair of parallel faces no	Indices h k l	Spacing/mm
---------------------------	------------------	------------

1	1 0 1	0.054
2	-1 0 1	0.062
3	0 -1 0	0.198

Crystal volume = $0.65 \cdot 10^{-3} \text{ mm}^3$

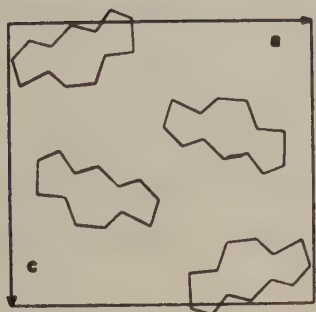
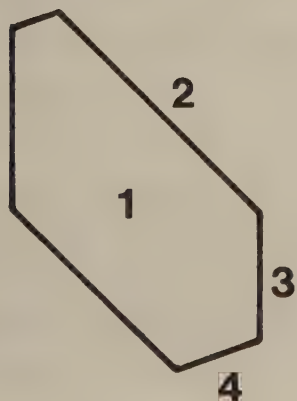


Fig. 2.2 The faces of a single crystal of B related to the unit cell and to the packing of molecules in it. The crystal is a needle elongated along b.



Pair of parallel faces no	Indices h k l	Spacing/mm
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1	1 0 0	0.25
2	0 1 0	0.11
3	0 -1 1	0.17
4	0 0 1	0.24

Crystal volume = $4.7 \cdot 10^{-3} \text{ mm}^3$

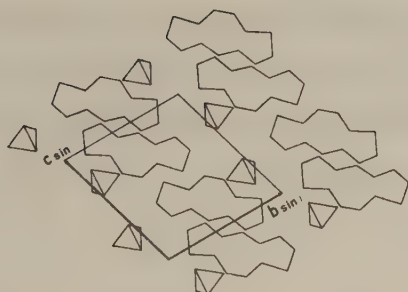


Fig. 2.3 The faces of a single crystal of E related to the unit cell and to the packing of molecules in it.

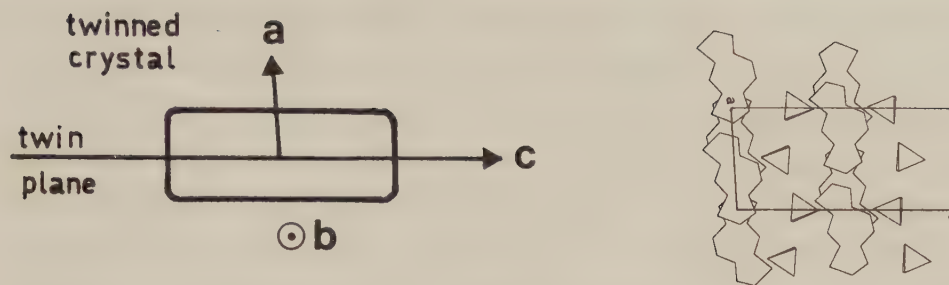


Fig. 2.4 Crystal habit of G I related to the unit cell and to the packing of molecules in it.

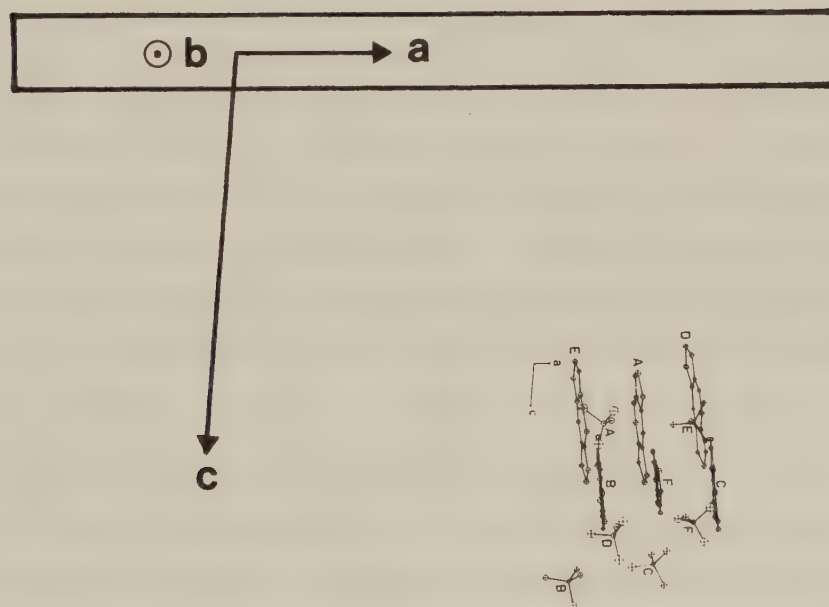


Fig. 2.5 Crystal habit of G II related to the unit cell and to the packing of molecules in it. One asymmetric unit of the unit cell is shown in the lower part of the figure.

2.5 Optical Properties

The present crystals are birefringent. The refractive index in any direction in a crystal is given by the indicatrix. The axes of the indicatrix are related by the symmetry of a crystal to those of the unit cell. For a monoclinic crystal one of the axes of the indicatrix coincides with the b-axis of the unit cell, and for a triclinic one there are no restrictions.

Indices related to structures. The refractive indices depend almost entirely on the individual molecules and the relative orientations of these molecules in the crystal (Bunn, 1961). The present molecules are relatively flat and of aromatic character. If they were all parallel in a crystal it would have very high refractive indices for vibrations in the plane of the molecules, and a low index normal to the plane. Such a crystal would be strongly negatively birefringent. It is a fact that in the present ionic compounds, there are flat roughly parallel cations.

Observed refractive indices. The principal refractive indices measured for $\text{G II} \cdot \text{ClO}_4^-$ are given in Table 2.7. As the crystals are flat needles lying on 0 1 0 (cf. Morphology), two of the indices were readily measured by the aid of liquids of known refractive indices. The crystal axes are here identified only by knowledge of the morphology of the crystals. There is however, no doubt that α is almost in the direction of $\underline{a}$, which is the lengthwise direction of needles (Fig. 2.6). By conoscopic observations and the aid of a compensator, it was found that the crystals are biaxial negative, with an observed angle of 52° between the optic axes. *From these results it can be concluded that there is one low index approximately in the direction of $\underline{a}$, and at right angle to this direction there are two much higher ones.* The remaining index can be calculated, knowing two refractive indices and the angle between the optic axes. Assuming that the β -axis of the indicatrix coincides with the b-axis of the unit cell gives $\beta = 1.65$. The accuracy of this calculated value is rather lower than for α and β . The other alternative, $\gamma // b$, gives an unreasonably high value of γ . Therefore $\beta // b$ is proposed and this orientation of the indicatrix is given in Fig. 2.6.

Comparison to the structure. The results of the determination of the crystal structure of G II show that the normals to the molecular planes are roughly parallel to a. In fact, they are inclined 3° to the a-axis (cf. Crystal Structure, Fig. 3.5). This is in excellent agreement with the observed direction of α relative to a. Moreover, the cations are rotated in different ways around their normals. It was tried to calculate the indicatrix from the structure (vide infra), and hereby to account for the various orientations mentioned. The result is given in Table 2.7 and Fig. 2.6 for comparison with the observed values. Even the direction of β relative to γ , which depends on the orientations of cations mentioned, agrees with the proposed directions. The magnitudes of the calculated values relative to the observed ones are discussed after the description of the calculations.

Pleochroism. The crystals of G II show pleochroism. They appear darker for light vibrating at right angle to a. Light vibrating in the plane of molecules is absorbed stronger than light vibrating in other directions. Thus, the effect of pleochroism is in accordance with the structure.

G I.ClO₄⁻. The crystals of G I.ClO₄⁻ are plates lying on 0 1 0. They are in general twinned. The lower of the two indices observed is in the length direction (Fig. 2.7). Using crystals on edge, it was found that they are biaxial negative with the observed angle of 25° between the optical axes. From these data the third index can be calculated. Also here the directions of β and γ are not known, but only one alternative agrees with the observed data. The proposed orientation is given in Fig. 2.7.

Comparison to the structure. In the structure of G I.ClO₄⁻ there are layers of cations in the ab-plane. The observed α -axis of the indicatrix form an angle of 4° to the c-axis (Fig. 2.7). In fact, the α -axis is directed at right angle to the layers. Thus, it seems as if the layers determine the orientation of the indicatrix. The cations have their normals inclined in two different directions to b (cf. Fig. 3.9). Calculations from the structure indicated that the α -index should be parallel to b (vide infra). This fact is not in agreement with the observed data.

Pleochroism. G I appears darker for light vibrating in the direction of a, which is in accordance with the structure.

E.BF₄⁻. Preliminary results for E indicate that there is a large difference between the highest and lowest refractive indices. The difference is comparable to that of G II (Table 2.7).

Calculations. There are a few methods to calculate refractive indices. Those applied here use the concept of atom polarizability (atomic refraction, Bragg, 1939) or bond polarizability. The refractive indices can be calculated for a liquid or for a crystal, in the latter case if the directions of molecules are known for it. For the present crystals, it was tried to calculate the mean of the refractive indices. *A liquid (or melt) of the same density as the crystal was assumed.* This means that the molecules have a random orientation, and atom polarizabilities for a molecule were summed up to give the calculated values in Table 2.8. These are compared to the observed average indices in the table.

Comparison to observed values. The average observed value for G I is much higher than the values for E and G II. The latter ones agree with the respective calculated values, which have been obtained assuming random orientation of molecules. The discrepancy for G I cannot be explained at present.

Crystal. In single crystals there are three different indices of refraction. To calculate them it is necessary to account for the directions of molecules in the crystal. Following Bunn (1961) bond polarizabilities were first added to give polarizabilities in the main direction of one molecule. The refractive indices in the main directions of molecules can be calculated from these molecular polarizabilities, if all molecules are thought to be parallel in a crystal (Table 2.9). By adding the molecular polarizabilities in the directions of extinction in the crystal, polarizabilities for these directions in the crystal were obtained. Values of the refractive indices were calculated from these and are given in Table 2.7.

Discussion of the calculations. The calculated refractive indices in the main directions of a molecule (Table 2.9) are largely influenced

by the choice of bond polarizabilities. Especially when bonds with S and Cl are involved. This choice alters the magnitude of the values calculated. Choosing delocalized bonds or localized double and single bonds even changes the values relative to each other. Thus the values are only approximative, and influence the result when used for calculating values for a crystal.

Comparison to observed values. G II. The observed refractive indices for crystals of G II are lower than the calculated ones, and β is much lower relative to α and γ . The β and γ values are directed in the plane of cations and their relative magnitude depends on the rotation of cations around their normals as mentioned above. The calculated values show a great similarity, due to the fact that ions are rotated in approximately all directions. The observed larger difference is therefore difficult to reproduce by calculations. It might be noted that there is disorder in this structure. The relative values of the refractive indices are, however, in accordance with the observed values, and the orientation of the indikatrix agree completely with the observed one.

G I. The observed refractive indices for G I are, in contrast, higher than the calculated ones. The observed indikatrix is quite different from the calculated one. The expected direction of α is in a direction approximately normal to the molecular planes, which is the direction of b. It is remarkable that the observed direction of α instead is at right angle to layers in the ac-plane. The arrangement of ions in layers might have some connection with this unexpected result.

Table 2.7 Observed and calculated values determining the indikatrix.

The principal refractive indices of α and γ were measured. The value of β could not be measured, and was calculated from the observed values of α , γ and $2V$. Ordinary light was used.

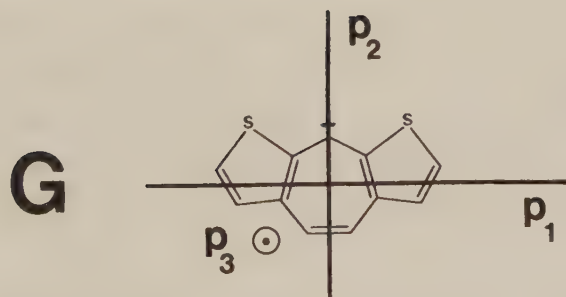
Crystal	Symmetry	Principal refractive indices			Birefringence Sign 2V (°)	Proposed orientation	
		α	β	γ		Principal axis axis of unit cell (°)	Plane of the optical axes
<u>Observed values</u>							
E	Triclinic	1.47	-	1.80			
G I.ClO ₄ ⁻	Monoclinic	1.80	(2.11)	2.2	-	α _{AC} = 4	Axial plane 1 0 1 0
G II.ClO ₄ ⁻	Monoclinic	1.53	(1.65)	1.92	-	α _{AA} = 4; z _{AC} = 8.5	Axial plane 1 0 1 0
<u>Values calculated from the structure</u>							
G I.ClO ₄ ⁻	Monoclinic	1.72	1.99	2.03	-	β _{AC} = 4	Axial plane // ab
G II.ClO ₄ ⁻	Monoclinic	1.58	2.08	2.13	-	α _{AA} = 3; z _{AC} = 7.5	Axial plane 1 0 1 0

Table 2.8 Calculated refractive indices. The concept of atom polarizability was used. Atomic refractions were added to give the molecular refraction (Getman, 1939). The atomic refraction for S was calculated from thiophene, for B from HBO_2 and for F from FCHCl_2 . The values are for a melt with the same density as the crystal of a substance. Localized double bonds were assumed.

Compound	Refractive index Calculated	Observed average $(\alpha + \gamma)/2$
E	1.66	1.64
G	1.72	G I 2.0 G II 1.73

Table 2.9 Calculated refractive indices in the main directions of a molecule. The values are those which, for these directions, would result in a crystal, if all molecules were parallel. Delocalized double bonds were assumed.

Compound	Main directions	Calculated refractive indices		
		n_{p_1}	n_{p_2}	n_{p_3}
G		2.25	2.0	1.6



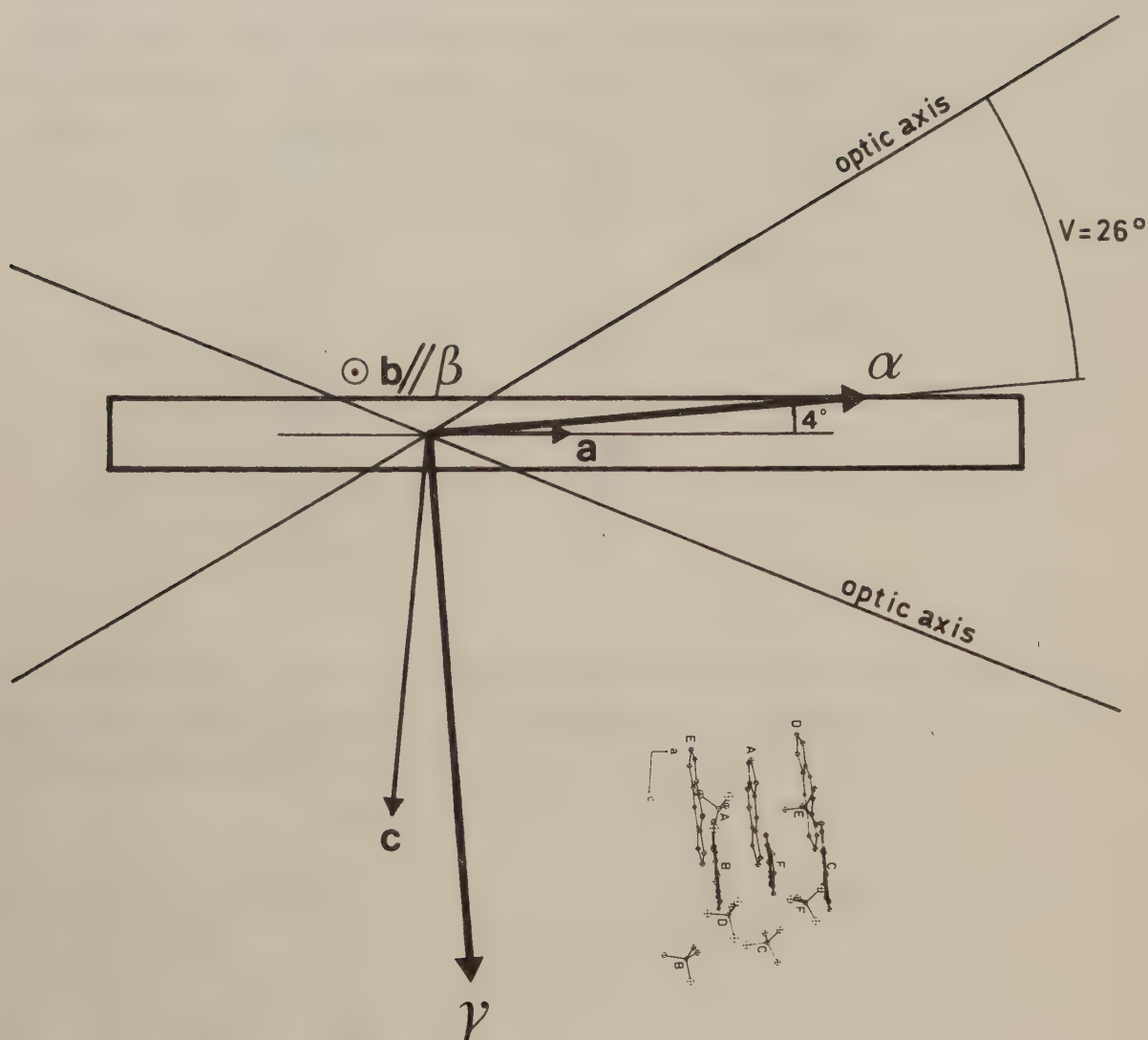


Fig. 2.6 The proposed orientation of the indicatrix relative to the axes of the unit cell for G II. ClO_4^- (cf. Table 2.7). $\underline{a}$, $\underline{b}$, $\underline{c}$ are the axes of the unit cell, and α , β , γ are the principal axes of the indicatrix. β is parallel to $\underline{b}$, and the optic axes are in the ac -plane. The angle between the optic axes is $2V$.

One asymmetric unit of the unit cell is given for comparison with the structure. The indicatrix calculated from the structure is as the proposed one, except that $\underline{a} \wedge \alpha = 3^\circ$ and $2V_{\text{calc}} = 14^\circ$.

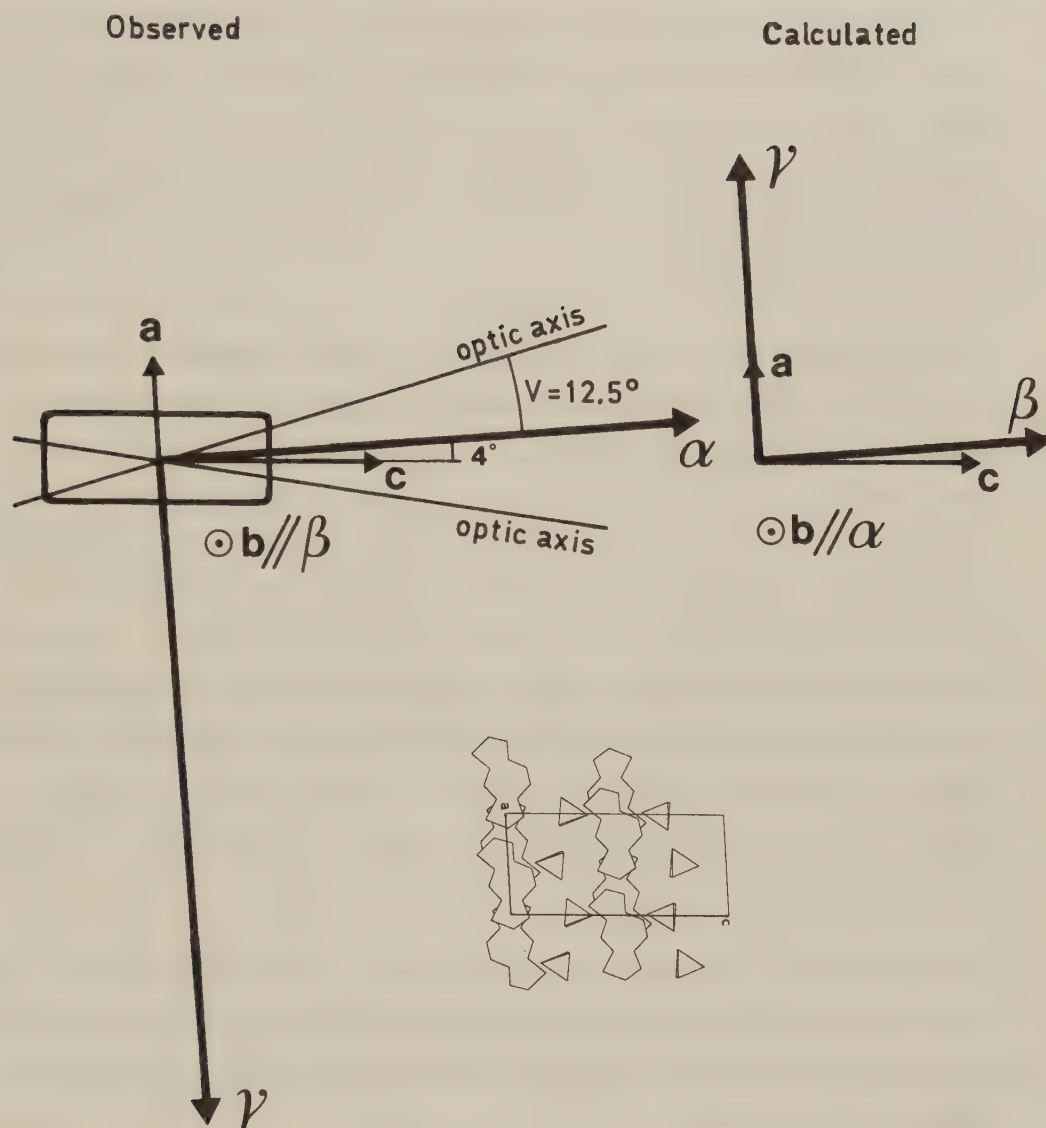


Fig. 2.7 The proposed orientation of the indicatrix relative to the axes of the unit cell for G I.ClO_4^- (cf. Table 2.7). The notations are as in Fig. 2.6. β is parallel to $\underline{b}$ and the optic axes are in the ac -plane. The angle between the optic axes is 25° . A view of the structure is given for comparison. The calculated indicatrix is given in the right part of the figure.

2.6 X-ray Diffraction Work

Different techniques have been used, due to the fact that the technical development has made it possible to make measurements of increasingly higher precision. Thus, the older photographic methods (Weissenberg technique), as well as modern counter methods (diffractometer technique) have been used. Data from all measurements have been summarized in Table 2.10.

Absorption. The single crystals used (cf. Preparative Work), were all controlled by Weissenberg recordings. Their size chosen were the largest attainable. In the first measurements CuK-radiation was used. Even though the absorption coefficient with this radiation is pretty low for the present substances, there is an appreciable absorption in the crystals. This fact makes a correction of the intensity data necessary, in order to attain the highest precision possible. In spite of a loss of intensity, MoK-radiation was used for the measurements later on, as due to low absorption, the absorption correction could be avoided. To gain intensity larger crystals were used, and were cooled to low temperature to minimize temperature motion. No extinction was noticeable.

Weissenberg recordings were made for the first structure (E Wb) and at two temperatures for G II. Cell dimensions and intensities were determined on a four-circle diffractometer (Enraf-Nonius CAD4) with equatorial geometry.

Monochromator. A graphite monochromator (discriminating the K β -radiation) was used, with two exceptions, as it gives higher intensity than a filter (2.8 times from comparison in G II). The detector was a scintillation counter.

Low temperature. The low temperature was achieved through a flow of cold nitrogen gas. In the outlet nozzle the outer parts of the laminar nitrogen flow was heated to prevent ice formation on the crystal. Moreover, the whole diffractometer was inclosed in a box filled with nitrogen (Danielsson, Grenthe & Oskarsson, 1976).

Crystal data. The diffractometer was used to determine the unit cell. This was also done with the powder technique. The θ -values of a number of reflexions were measured, and the cell dimensions calculated by least-squares. A high precision is often obtained, due to correctly indexed θ -values of high precision. However, it has often been demonstrated a significant difference between cell dimensions obtained by using diffractometer and by powder methods (Guinier-Hägg focusing camera). It should be noted that the former results are based on only one single crystal, and that there are systematic errors involved in both methods. A difference of about 2σ in cell axes is not uncommon. The Laue symmetry was determined from preliminary Weissenberg photographs. These are also important to ensure that the correct cell is chosen.

Determination of the intensities. The reflexions were scanned in the ω - 2θ mode, with a scan interval which was somewhat larger for increasing θ -values. It was noticed later, that a neighbouring reflexion could come into a scan for the 0k0 and 00l reflexions of compound G II. The reason is, that these reflexions are very closely spaced due to the long b- and c-axes. This makes the background unequal, greatly influencing the intensity value. The approximate scan time, which was needed to give a relatively high counting precision in reasonable time, was determined in a fast prescan. However, for very strong reflexions the number of counts were higher even though the shortest scan time was used. Correspondingly, for very weak reflexions the number of counts were lower as the maximum scan time was limited. Profile analysis was performed for one of the crystals (cf. article E).

Reflexions were collected only for the minimum part of the reciprocal sphere, but to as large a value of $\sin\theta/\lambda$ as reasonable. Those, which had an intensity less than two or three times their standard deviation, were considered as unobserved. The ratio of observed to unobserved reflexions are widely different for the recordings. Where CuK-radiation is used, the ratios are overall higher than with MoK-radiation, in spite of the higher temperature. Considering collections using the same radiation, the differences found are probably due to differences in crystal volume. Disorder of some kind in the crystal might be indicated by this ratio, e. g. G II compared to E at 143 K.

36 Table 2.10

X-ray diffraction work	Substance	B 295 K	A 173 K
<u>Absorption</u>			
Crystal size (mm^{-1})		$0.2 \times 0.054 \times 0.062$	$0.07 \times 0.07 \times 0.20$
Measuring order		2	4
Volume (mm^{-3})		$0.65 \cdot 10^{-3}$	$1.0 \cdot 10^{-3}$
Radiation ($\text{\AA}$)		1.5418	0.71073
Absorption coeff. (mm^{-1})		4.3	0.53
Transmission factor		0.64-0.82	-
<u>Monochromator-Filter</u>		graphite monochromator	graphite monochromator
<u>Crystal data</u>			
Number of reflexions on diff. θ -values measured		30	45
Laue symmetry; Wb-diff.		Orthorhombic, $\text{Pn}2_1\text{a}$	Monoclinic/ $\text{P}2_1/\text{c}$
Volume ($\text{\AA}^3$)/Z		1004.7/4	907.2/4
D_m/D_x (Mg m^{-3})		1.43/1.46	1.54/1.60
Crystal number		1	1
<u>Scan</u>			
Mode		$\omega/2\theta$	$\omega-2\theta$
Interval ($\Delta\omega$) $^\circ$		$(1+0.15\tan\theta)$	$(0.90 + 0.50\tan\theta)$
Prescan $\rightarrow$ total count of (cps)/(approx. count. precision) (%)		3000/1.8	3000/-
Part of rec. sphere/ θ -range ($^\circ$)		$\frac{1}{8}/3-75$	$\frac{1}{4}/3-27$
Total number of reflexions		1166	2142
Number of unobserved refl./ $I < x \cdot \sigma(I)$		$123/I < 2\sigma(I)$	$1007/I < 2\sigma_c(I)$
Number of observed refl./Tot. refl.		0.89	0.53
Number of int. control refl./Exp. time (h)		3/100	3/84
Total count of int. refl./Count. precis. (%)			10000/1
Estimation of real pre- cision of I/Decay (%)		- /4	2-5/0

E			G II		
Wb 295 K	295 K	143 K	1) 173 K	3) 173 K	Diff. 295 K
		0.25×0.17×0.11	0.3×0.2×0.1		
1	3	7	5	6	
$3.0 \cdot 10^{-3}$	$0.77 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$		$6.0 \cdot 10^{-3}$	
1.5418	1.5418	0.71073		0.71073	
4.4	4.4	0.48		0.66	
0.43-0.77	0.61-0.81	- (max 7%)		-	
Ni-filter	graph. monochr.	Zr-filter	graph. monochr.	Zr-filter	
	44	89		50	
Triclinic, P $\bar{1}$	Triclinic, P $\bar{1}$	Triclinic, P $\bar{1}$	Monoclinic, P2 $_1$ /c		
577.1	563.82/2	575.36/2	7210(3)/24		$\frac{7283(3)}{24}$
1.66/-	1.66/1.67		1.7/1.66		
1	2	3	1		
	ω -2 θ	ω -2 θ	ω -2 θ		
	(0.80+0.50tan θ)	(0.90+0.50tan θ)	(0.90+0.50tan θ)		
		- /2.2 (profile analysis)	3000/-		
c; 0-5 zon	$\frac{1}{2}/5-70$	$\frac{1}{2}/3-27$	$\frac{1}{4}/3-21$ (sin θ / λ = 0.079-0.50)		
1358	2320	2362	7410		
578	533/I < 3 σ_c (I)	910/I < 2 σ_c (I)	3616/I < 3 σ_c (I)		
0.57	0.77(3 σ)	0.61	0.51 (3 σ)		
	2/78	3/-	3/-		
		/1	10000/1		
		2-3/0	×1.5 σ /0 (only for one refl.)		

The intensities of a few control reflexions were recorded to follow crystal decomposition and instability of the equipment. An intensity decrease is given in per cent of the starting value (decay %). The control reflexions were measured to a precision of 1 % (total count of 10 000). The actual statistical distribution of the measured intensities was compared to a normal distribution by the normal probability plot method (Hamilton, 1974). The standard deviations of the intensity was in general underestimated, i. e. larger than 1 %, probably due to instabilities of some kind. The orientation of the crystal was checked regularly by an orientation control reflexion.

2.7 Determination and Refinement of the Structures

Corrections. The intensities collected are here used for calculating the positions of atoms in the unit cell (Table 2.11). The intensities were corrected for Lorentz and polarization effects, and in some cases for absorption.

Space group. Crystal system and systematic extinctions were inferred from Weissenberg photographs, recorded at room temperature. For the low temperature intensities, the systematic extinctions were checked by inspection of the intensity data. No phase transition was observed. For B and E the space group was ambivalent. For B and E the space group was ambivalent. E-statistics strongly indicated the presence of a center of symmetry for E, and absence more vaguely for B. Least-squares refinement was performed also in Pnma to verify this.

The heavier atoms were found from vector maps or by performing symbolic addition. Subsequent electron density syntheses and least-squares refinements gave the positions of all atoms, except in some cases hydrogen atoms. In E two different orientations of the BF_4^- -ion were found, and in G II the positions of some O-atoms were uncertain, due to disorder of ClO_4^- -ions. Probably additional orientations were possible also for this compound.

Least-squares. In the final full-matrix least-squares refinements, the function minimized was $\sum w(\Delta|F|)^2$, where $\Delta|F| = |F_o| - |F_c|$. The weight function was $w^{-1} = \sigma_c^2(|F_o|) + C1 \cdot |F_o|^2 + C2$. The scattering factors used were the same for all compounds (cf. articles). Correction

for anomalous scattering was particularly important for B, as space group $Pn2_1a$ has a polar axis. By neglecting the imaginary component of the anomalous scattering serious errors in the positional parameters along this axis might result, even for light elements (Cruickshank & MacDonald, 1967). However, the refinements did not show that this correction had improved the fit.

Parameters. Hydrogen atoms were not refined for G II. The BF_4^- -ion was inserted in two different orientations, the occupancy factors (sum = 1) of which were refined relative to each other. Anisotropic temperature factors were refined for non-hydrogen atoms, with some exceptions. These atoms were treated isotropically in order to limit the number of parameters. For G II all parameters could not be refined simultaneously.

Agreement. The final values of the agreement indices for E reflect the measuring method used, and the importance of a low temperature. G II has a large value due to disorder, and that of E is probably also affected by disorder. There is a large difference for E between room- and low-temperature. However, B has even lower agreement indices than A, in spite of the higher temperature. It might be possible that the molecules in B are more restricted in their thermal movements, possibly due to the crystal packing. A rigid body calculation indicate that movements of molecules are large in E, making the influence of temperature very large. Generally, a better fit was obtained when using anisotropic temperature factors instead of isotropic ones. It was not tried to manipulate the S-value too much by changing the constants in the weighing function.

As mentioned earlier, the fit for B was not improved when using anomalous scattering factors. There is a large difference, though, between the R-values of the two enantiomorphs. The final refinements for B were performed in exactly the same way. One possible explanation to this (Samson, private comm.) is that the crystal is a twin with the polar axes parallel to each other but directed in opposite direction. It should also be remembered, that there is only a very slight deviation from centrosymmetry.

Table 2.11

Determination and refinement of the structures	Substance	
	B 295 K	A 173 K
<u>Corrections of int.</u>		
Absorption/transm. factors	Yes/0.64-0.82	No/-
<u>Space group</u>		
Systematic extinctions	hk0:h=2n+1 0k1:k+1=2n+1	h0l:l=2n+1 0k0:k=2n+1
Characteristic space groups	Pn2 ₁ a, Pnma	
E-statistics indicate	Pn2 ₁ a	
Space group	Pn2 ₁ a	P2 ₁ /c
<u>Method of solving</u>		
Vector map (atoms found)		Vector map (S-atoms)
Symb. add., (atoms re- vealed, (Program)	S. a., (S-atoms), (GAASA)	
<u>Least-squares refinement</u>		
Fullmatrix, $\Sigma w(\Delta F)^2$ minimized		
Weight function (C1; C2) $w^{-1} = \sigma_c^2 (F_o) + C1 \cdot F_o ^2 + C2$	0.0006; 0.1	0.000625; 0.10
Scattering factors	S-O-C; H; Anom. sc. f.	S-O-C; H; Anom. sc. f.
Parameters		
atoms (remarks)		
temperature factors, anisotropic/isotropic	S-C/H	S-C/H
Agreement indices R/R _w	0.0363/0.0446	0.041/0.044
S	1.01	1.03
R ₁ /R ₂ /S Corr. for anom-	0.0371/0.0453/1.03	
R ₁ /R ₂ /S alous scattering	0.0453/0.0567/1.35	
Residual el. density (e Å ⁻³)		0.31
Extinction correction	No	No
Rigid body		Not successful
Scale factor	0.981	4.34
<u>Overall temperature factor</u>		
mean t.f. S: $10^4 \cdot \frac{U_{11} + U_{22} + U_{33}}{3} \text{ Å}^2$	640	340
Number of parameters	158	152
<u>Number of reflexions</u>	6.59	7.47
Number of parameters		
σ_c (position) (Å)	0.006	0.005

E			G II	
Wb 295 K	295 K	143 K	1) 173 K	3) 173 K
Yes/	Yes/0.61-0.81	No/-	No/-	
			h01:l=2n+1 0k0:k=2n+1	
P1, P $\bar{1}$				
$\frac{P1}{P\bar{1}}$			P2 ₁ /c	
Vector map (S)			-	
S. a., (S), (G)			S. a., (S, C1), (MULTAN)	
			Not simultaneous refinement	
7.0; 0.02 (Cruickshank)	0.0016; 0.30	0.0016; 0.30	0.000625; 0.10	
S-B; H;	S-C; H; Anom. sc. f.	S-B; H; Anom. sc. f.	C1-C; -; -	
One orient.	BF $\bar{4}$ - two diff. orient. (0.75-0.25)	BF $\bar{4}$ - two diff. orient. (0.64-0.26)	Not H-atoms; C10 $\bar{4}$ only one orient.	
S-B/H	S-C-B/F-H (4.5 Å ²)	$\frac{S-C-B/F-H}{S/F-H}$	S/C1-O-C	
0.117/0.161	0.084/0.111	$\frac{0.043/0.057}{0.048/0.063}$	0.122/0.164	
0.55	1.45	1.01/1.09	1.01	
-	0.95 (BF $\bar{4}$)	0.28 (cation)	1.65	
No	No	0.67 (BF $\bar{4}$) No	No	
-	Successful	Successful	-	
MV 0.31	0.410	1.334	15.05	24.68
	580	270	400	
191	182	189	494	
4.06	9.82	7.66	7.95	
0.025	0.007	0.005	0.030	

Another measure of the fit of the model is the residual electron density. This is larger for the structures with disorder. In maps of residual electron density the disorder of BF_4^- and ClO_4^- is evident. In A there is apparently features, which the model cannot account for, such as π -orbitals. Some maps are shown under the heading of Crystal Structure, disorder. For extinction cf. X-ray Diffraction Work.

CRYSTAL STRUCTURE

3. CRYSTAL STRUCTURE

3.1 Description of the Structures

Besides compounds determined by the author (B, A, E, G II), a compound determined by Aurivillius (1974) will be used to compare structures. Schematic pictures of the structures are given in Figs. 3.1-5 and stereoviews in Figs. 3.6-10. Two of the compounds (B, A) are composed of molecules, giving molecular crystals. The molecules are cyclic ketones (cyclohepta dithiophenes), with the only difference that B has one double bond less than A (cf. Introduction). The other compounds (E, G I, G II) are composed of ions, giving ionic crystals. The cations are cycloheptadithiophenylum ions (tropylium ions); the one in E is very similar to the molecules B and A, and the one in G I and G II differ just by the positions of the S atoms (cf. Introduction). The anions are BF_4^- in compound E and ClO_4^- in G I and G II.

Crystal system. The crystals belong to the orthorhombic, monoclinic and triclinic crystal systems. Some crystal data are given in Table 3.1. The crystal of B has a polar axis and the other ones are centrosymmetric. In the unit cells of all the structures except G II, there is only one independent unit, consisting of a molecule or cation-anion pair, which is repeated by symmetry in the unit cell. G II, in contrast, has six independent units. In no one of the structures, any of the molecules or ions are positioned in such a way in the unit cell that symmetry elements of the molecule coincide with crystallographic ones.

Structural arrangement. Some regularities can be imagined when studying the structures. B can be thought of as built up of somewhat tilted molecules, piled up in the direction of the b-axis. A can formally be thought of as composed of pairs of molecules, related by a center of symmetry. E and G I show layers which are parallel to the ac- and ab-planes respectively. G II has columns of cations with the axes of the columns parallel to a. All cations in E are parallel to each other. In G I the cations are parallel within each of two layers, the layers being related by screw diads. The cations in G II have their normals roughly in the direction of the a-axis. The anions are disordered in the ionic structures, and in G II probably also the cations to some extent.

Table 3.1 Crystal data for compounds B, A, E.BF₄⁻, G I.ClO₄⁻ and G II.ClO₄⁻. Data for G I are given by Aurivillius (1974). For cell data at room temperature cf. articles.

B	$C_{11}H_8OS_2$, MW 220.3, orthorhombic, space group $Pn2_1a$			
	$a = 15.1520(5) \text{ \AA}$	$V = 1004.7 \text{ \AA}^3$		
	$b = 4.6668(2)$	$Z = 4$		
	$c = 14.2083(5)$	$T = 295 \text{ K}$		
A	$C_{11}H_6OS_2$, FW 218.30, monoclinic, space group $P2_1/c$			
	$a = 9.3331(13) \text{ \AA}$	$\beta = 110.098(14)^\circ$	$T = 173 \text{ K}$	
	$b = 8.6930(18)$	$V = 907.18 \text{ \AA}^3$		
	$c = 11.9065(26)$	$Z = 4$		
E	$(C_{11}H_7S_2)^+BF_4^-$, FW 290.1, triclinic, space group $P\bar{1}$			
	$a = 7.1949(12) \text{ \AA}$	$\alpha = 105.787(15)^\circ$	$V = 563.82 \text{ \AA}^3$	
	$b = 8.7203(12)$	$\beta = 99.074(13)$	$Z = 2$	
	$c = 9.5967(20)$	$\gamma = 96.817(13)$	$T = 143 \text{ K}$	
G I	$(C_{11}H_7S_2)^+ClO_4^-$, FW 302.7, monoclinic, space group $P2_1/n$			
	$a = 6.819(2) \text{ \AA}$	$Z = 4$		
	$b = 12.032(4)$	$D_m = 1.79 \text{ g cm}^{-3}$		
	$c = 14.677(6)$	$D_x = 1.68 \text{ g cm}^{-3}$		
	$\beta = 93.60(3)^\circ$	$\mu(\text{CuK}\alpha) = 64.0$		
	$V = 1201(1) \text{ \AA}^3$	$T = 295 \text{ K}$		
G II	$(C_{11}H_7S_2)^+ClO_4^-$, FW 302.8, monoclinic, space group $P2_1/c$			
	$a = 10.4615(18) \text{ \AA}$	$\beta = 94.657(10)^\circ$	$T = 173 \text{ K}$	
	$b = 25.7202(26)$	$V = 7210(3) \text{ \AA}^3$		
	$c = 26.8840(23)$	$Z = 24$		

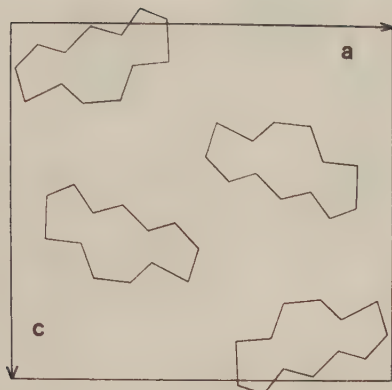


Fig. 3.1 Structure B

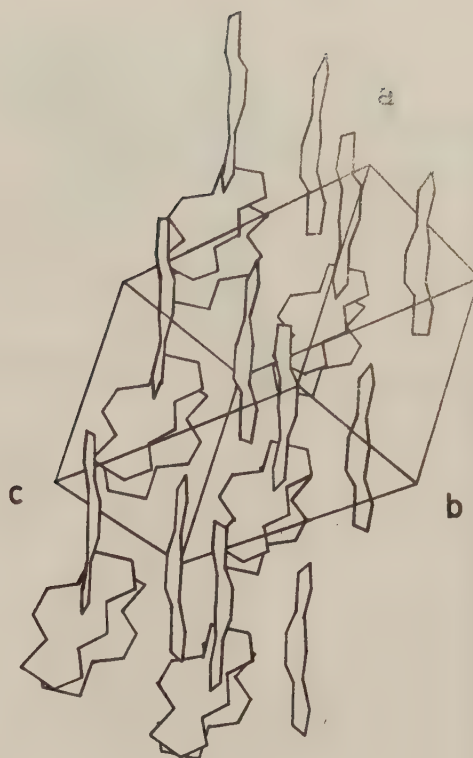


Fig. 3.2 Structure A

Fig. 3.1 A projection of B with the b-axis pointing towards the reader. One unit cell and the molecules in it are shown.

Fig. 3.2 A view of the stacking of molecules in A.

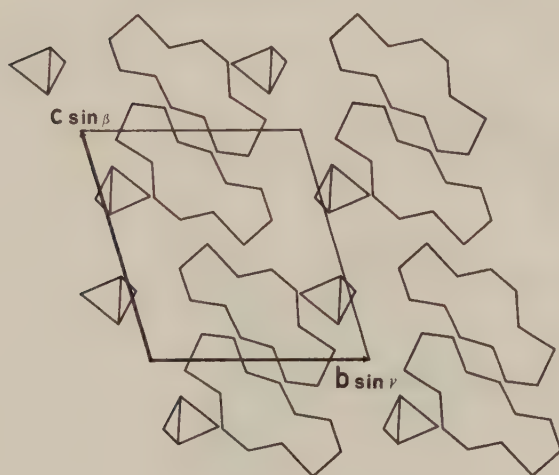


Fig. 3.3 Structure E

Fig. 3.3 A projection of E with a pointing towards the reader.

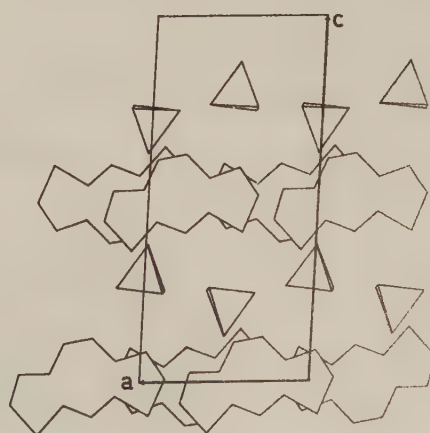


Fig. 3.4 Structure G I

Fig. 3.4 A projection of G I with b pointing towards the reader.

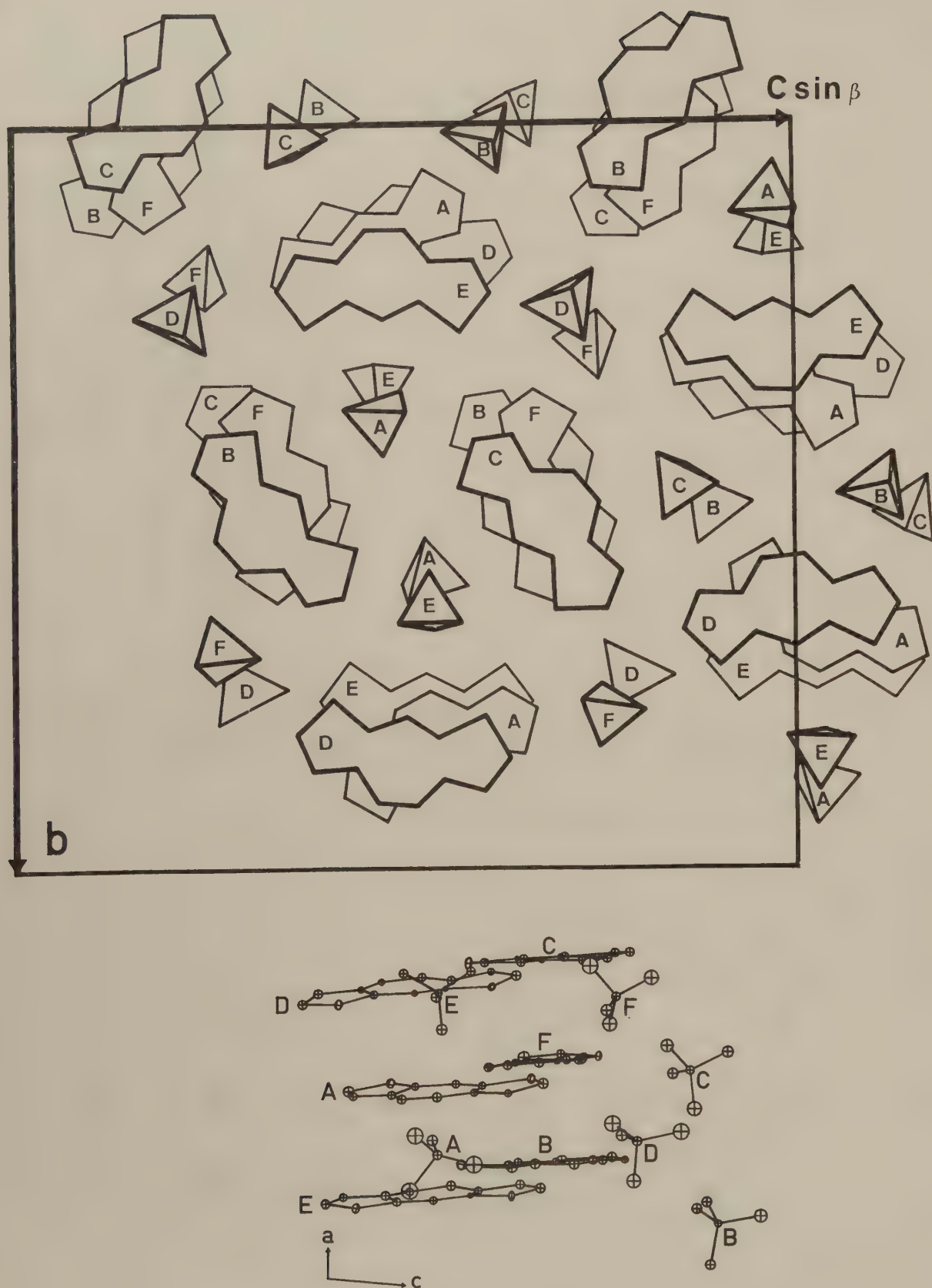


Fig. 3.5 Upper part. A projection of one unit cell of G II with $\underline{a}$ pointing towards the reader. Lower part. A projection of the asymmetric unit of G II in the direction of $\underline{b}$.

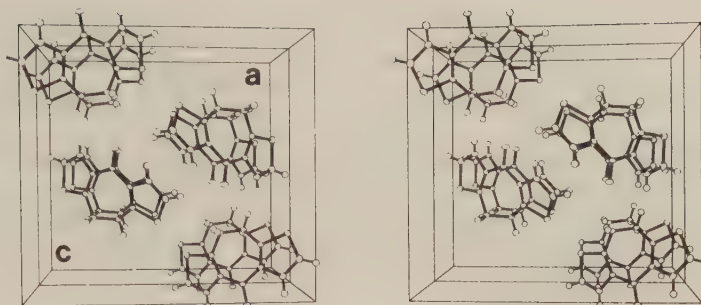


Fig. 3.6 A stereoview of two unit cells of B. 11 % probability ellipsoids are drawn (295 K).

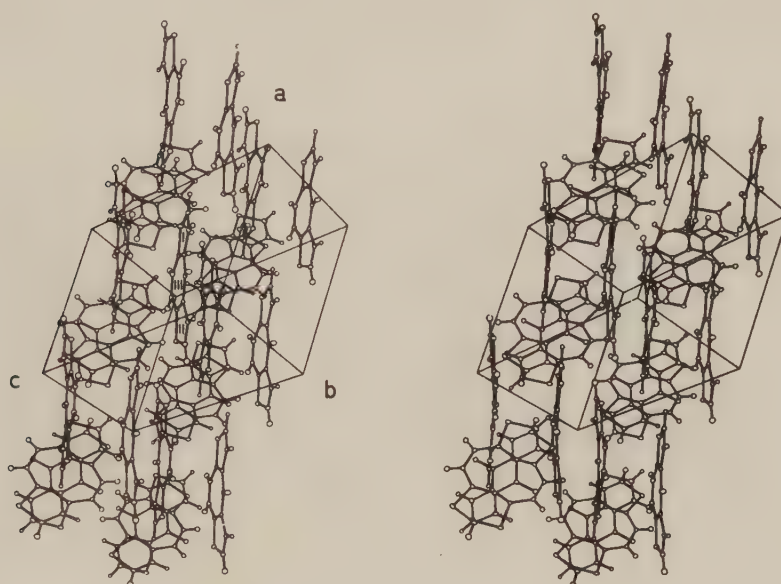


Fig. 3.7 A stereoview of the stacking of molecules A. The rings of the molecule in the asymmetric part of the unit cell are marked according to Fig. 4.7 (173 K).

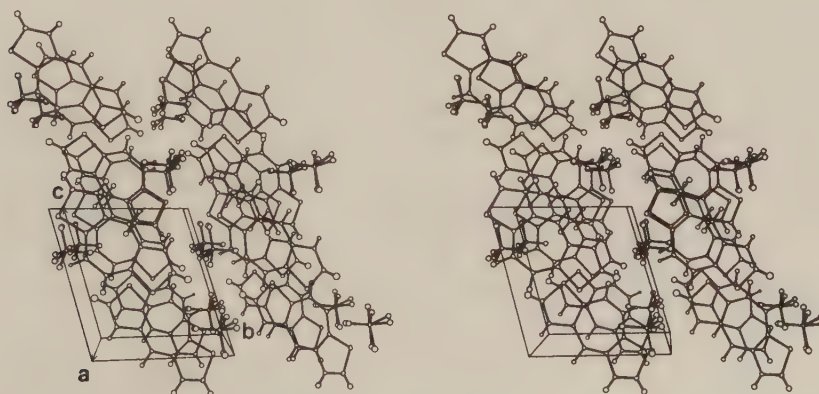


Fig. 3.8 (a) A stereoview of the stacking of ions E at 143 K with a pointing towards the reader.

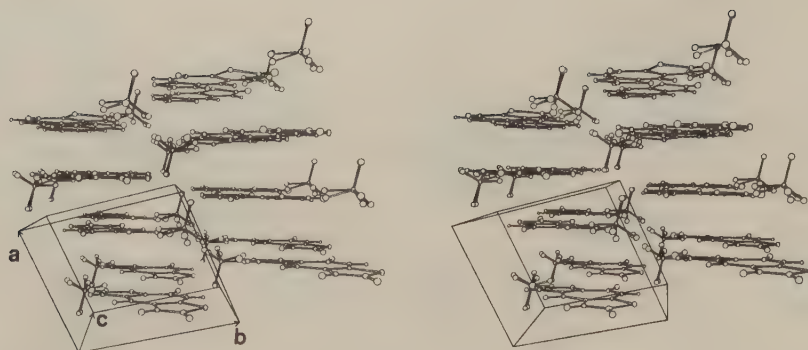


Fig. 3.8 (b) A view of the stacking of ions E at 143 K with the planes of cations seen from the side.

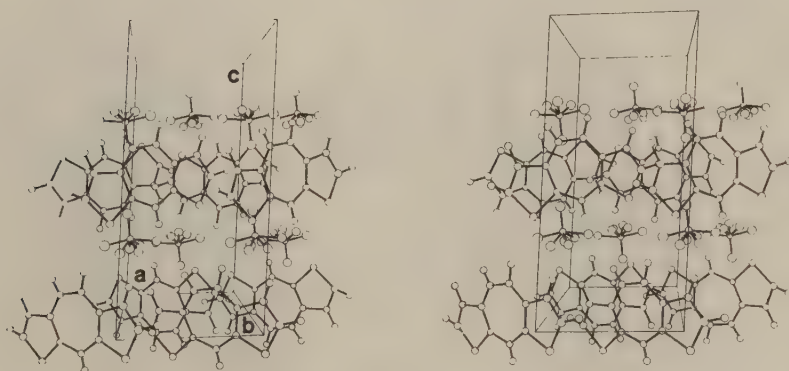


Fig. 3.9 A stereoview of G I. b is pointing towards the reader (295 K).

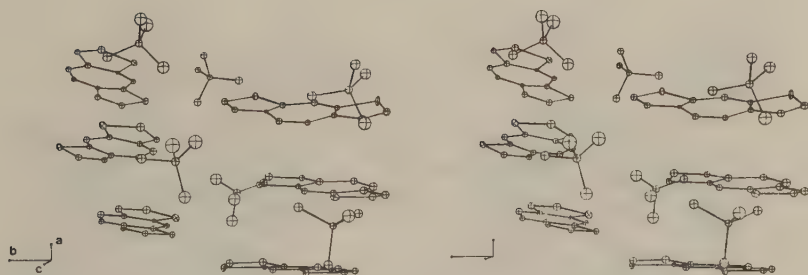


Fig. 3.10 A stereoview of the asymmetric unit of G II (173 K).

3.2 Short Contacts Between Molecules or Ions

Short contacts. The shortest distances between molecules or ions in the present compounds are compared between the compounds and to the van der Waals distances. The van der Waals surfaces of cations E and G are shown in Fig. 3.11. The structures can be thought of as constructed by putting together building units of a shape given by their van der Waals surfaces, so that they are in close contact with each other. The short contacts between ions will be discussed in the order distances between cations or molecules, between anions and between anions and cations. The distances, which are about the length of the corresponding van der Waals distance or less, are given in Table 3.2.

Cations-cations. The van der Waals contacts are mainly between atoms S...H, O...H, C...H and C...C. The reason that hydrogen atoms are involved in most close contacts is that the ions (or molecules) have peripheral hydrogen atoms (cf. Fig 3.11). Short C-C contacts can occur if molecules turn their flat sides against each other. Between sulphur atoms, there are only one van der Waals contact. The reason is that the cations are large and with only two sulphur atoms. Therefore, it depends on how the units are packed, whether sulphur atoms come into close contact to each other or not.

Layers. The short contacts between molecules of A are only partly within the pairs, related by a center of symmetry. *For E and G I they are within layers of cations, and for G II mostly within columns (one exception).* The layers seen at right angle to the best planes of cations (or molecules) are presented in Fig. 3.12. The ions (or molecules) overlap each other, but are placed in such a way that, with some exceptions, the atoms do not fall straight over each other. *The atoms which do fall straight over each other form the short contacts mentioned above for E and G I.* The distances between the best planes are given. It should be noted that the molecules are not quite planar, there is a small angle between the thiophene planes (cf. Molecular Structure, Fig. 4.1-5). In E, the distances between planes are shorter than the shortest contacts, which probably is made possible by the fact that the cation is not quite planar. In A there are short contacts also outside the pairs, and in G II also one S-S contact between columns.

Range of contacts. Generally, there are only a few C-C contacts which are about the van der Waals distance. There is often a gap, the next nearest distances are somewhat longer (Table 3.3). This is quite pronounced for E, and is probably due to the fact that the contacts are within layers and between parallel ions. *Just a few of the carbon atoms fall straight over each other, giving van der Waals contacts, due to the relative orientation of the overlapping cations.*

Anions-anions. Contact distances between anions are quite long (Table 3.2). There is only one van der Waals contact (compound E), and this is within a layer of anions. *The fact that the cation is large relative to the anion, probably causes the anions to be well separated from each other in general.*

Anions-cations. Distances between ions of different charge are short relative to the van der Waals distances (Table 3.2). E and G I have some very short O,F-S distances in contrast to G II, which has 3.17 Å as its shortest distance. 3.17 Å seems to be the van der Waals distance to be assumed, as it is a lower limit for the distance also for E and G I, with only a few rather short distances as mentioned above. For distances O,F-C there is a very short contact also for G II, but for G I there is no quite short one. Also here, there is a gap between the very short distances and the presumed van der Waals distance, here probably 3.15 Å.

O,F-H. O,F-H distances are short, one short in A and a whole series in E and G I. The shortest one is 2.3 Å (F...H-C), and the angles F,O,S...H-C are from 140 to 163°. The short distances are probably not hydrogen bonds. The situation is similar in G I. H atoms were not determined in G II.

Attractive forces. It might be noted that the shortest O-H contact for A is in between the ones of B and E. The polarization of the carbonyl bond (cf. Introduction) makes the O atom of A more negatively charged than B, i. e. the charge is in between that of B and the anions. *The reasoning above indicate that attractive forces between ions of different charge is the reason for, relative to the van der Waals distances, the rather short contacts between anions and cations.*

Molar volume. The packing density for the structures are given in Table 3.4. The values show that E has a denser packing than both structures of G. G II with the highest degree of disorder has the lowest packing density. The packing coefficient (Kitaigorodsky, 1973) is also given. It is the quotient between calculated and measured volume of a molecule. It is larger for $G I.I^{-}$ than for $G I.ClO_4^{-}$.

Conclusion. The present ionic compounds, G I and G II, are layer structures and G II is a columnar structure. Short contacts between cations are mainly within layers or columns of cations. The layers or columns are kept together by anions having short distances to the cation layers. The anions are in general well separated from each other.

Table 3.2 The shortest distances between molecules or ions (Å) in the present compounds. The distances are compared to the corresponding van der Waals distances (VdW). The van der Waals radii, given by Bondi (1964), have been used to calculate the distance between atoms which are in van der Waals contact to each other.

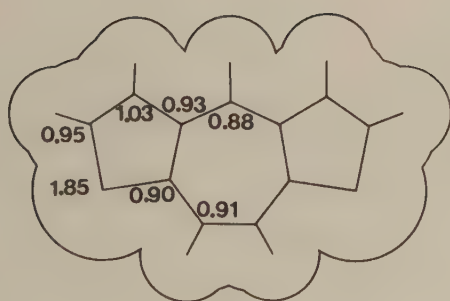
	VdW	B	A	E	G I	G II
		Molecule-molecule		Cation-cation		
S...S	3.5	3.723(4)	3.871(2)	3.650(2)	3.716(4)	3.49(2)
S...O	3.25	>4.0	3.345(3)			
S...C	3.45	3.817(7)	3.508(4)	3.573(4)	3.563(12)	3.34(4)
S...H	2.95	3.01(7)	3.03(4)	3.07(6)	3.06(13)	-
O...O	3.0	>4.0	>4.0			
O...C	3.2	3.272(7)	3.349(5)			
O...H	2.7	2.64(7)	2.42(5)			
C...C	3.4	3.575(9)	3.422(6)	3.428(5)	3.426(16)	3.40(4)
C...H	2.9	2.93(5)	2.85(4)	3.05(5)	3.21(14)	-
H...H	2.4	2.65(8)	2.50(6)	2.82(8)	2.34(28)	-
				Anion-anion		
O...O	3.0	>4.0	>4.0		3.709(24)	3.34(5)
F...F	3.0			3.027(18)		
				Anion-cation		
O...S	3.25	>4.0	3.345(3)		3.028(25)	3.17(4)
F...S	3.25			3.020(10)		
O...C	3.2	3.272(7)	3.349(5)		3.058(43)	2.97(4)
F...C	3.2			2.950(11)		
O...H	2.7	2.64(7)	2.42(5)		2.31(15)	-
F...H	2.7			2.30(5)		

Table 3.3 Carbon-carbon distances between molecules or cations in the present compounds.

Compound	Number of atoms in a specific molecule which have van der Waals contacts to other mol- ecules	Contact distances			Comment
		Range of van der Waals con- tacts		minium distance outside min-max	
		min	max		
Molecule-molecule					
B	-	-	-	3.575(9)	
A	5	3.422(6)	3.447(5)	3.505(5)	both within and without pairs
Cation-cation					
E	5	3.428(5)	3.447(7)	3.593(6)	within layers
G I	2	3.426(16)	3.426(16)	3.497(16)	within layers
G II	-	3.40(4)	-	-	within layers

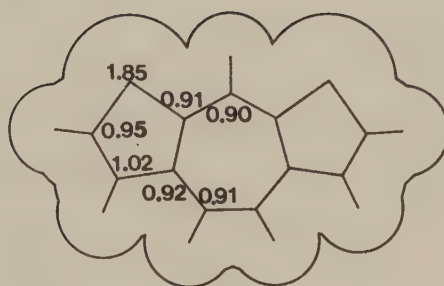
Table 3.4 Packing density of crystals (295 K). The volume per formula unit ($\text{\AA}^3$), density (Mg m^{-3}) (calculated) and packing coefficient (Kitaigorodsky, 1973) are given.

Compound	Vol./f.u. ($\text{\AA}^3$)	Density (Mg m^{-3})	P.c.
B	251.2(1)	1.46	0.70
A	231.3(2)	1.57	0.74
E.C10 ₄ ⁻	291.9(2)	1.72	0.73
G I.C10 ₄ ⁻	300.3(4)	1.68	0.71
G II.C10 ₄ ⁻	303.4(2)	1.66	0.70
E.BF ₄ ⁻	287.7(1)	1.67	0.73
G I.I ⁻	287.8(9)	1.90	0.73



E

a)



G

b)

Fig. 3.11 Van der Waals surfaces for a) cation E and b) cation G. The electron density obtained by MO-calculations is given.

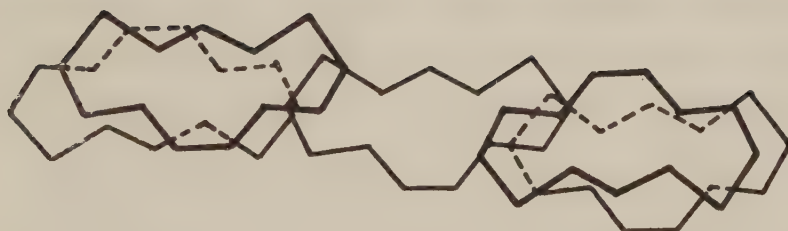
Distance between best planes	Tempera- ture of the structure determination	
3.54 Å	173 K	A
3.347 Å 3.378 Å	143 K 295 K	E
3.443 Å	295 K	G I
≈3.476 Å ≈3.507 Å	173 K 295 K	G II



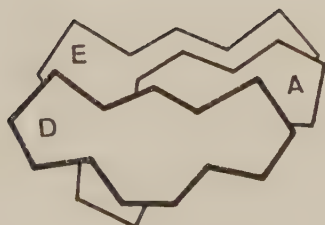
3.54 Å 173 K **A**



3.347 Å 143 K
3.378 Å 295 K **E**



3.443 Å 295 K **G I**



≈3.476 Å 173 K
≈3.507 Å 295 K **G II**

Fig. 3.12 Overlap of cations and molecules. Projections at right angle to the best planes of molecules. A pair (A), layers (E, G I) and columns (G II) are shown.

3.3 Coordination

Coordination of cations to anions. E and G I. From the shortest distances to cations (Table 3.5 and Fig. 3.13) it is concluded that in E one anion is surrounded by eight cations. Seven of them are in close contact with the BF_4^- ion, and the eighth are at a slightly longer distance (no. 6). Next molecule has a distance longer than 4 Å. In G I there are also eight cations around one anion (cf. Fig. 3.14). Cations 2 and 4 have only H atoms in contact with ClO_4^- . The view of the van der Waals surface of the cations (Fig. 3.11) show that the contacts in the plane of a cation will be to hydrogen atoms. The two cations in G I, mentioned above, have the nearest O atom in their planes, and this explain why there are no van der Waals contacts (C-O) to the carbon atoms of these cations. Both in E and G II the anion is surrounded by cations, which have the anion in their best planes, and so there are (mainly) short contacts to hydrogen atoms and also to S atoms (Table 3.5).

G II. In G II there are 6 independent anions. Anions A,E and B,C are surrounded by three columns of cations and D,F by four columns (cf. Fig. 3.5). In many cases the anion considered is situated near the best plane of one of the cations of a column. In this case there can be contacts to sulphur or hydrogen atoms; carbon atoms are shielded by hydrogen atoms. Distances to carbon atoms therefore, for this case, should be longer than the van der Waals distance and are accordingly in G II about 3.3 Å (Table 3.5). When the anion is far from the best plane, direct contacts to carbon atoms can be expected; the shortest contact is 2.97(4) Å. A ClO_4^- ion can have contacts to one, two or even three of the cations of a column. A is in contact with 3 cations, B,C with 4, E with 5, D with 6 and F with 7 cations. The next nearest cations are often pretty close, about 3.4 Å (C-C).

A, D and F are disordered. D and F are coordinated to a relatively large number of cations, which also have their ends turned towards the ClO_4^- ion.

Coordination of anions to cations. E. The coordination of anions to cations is related by symmetry to the coordination of anions described above. Thus, the cation E (Fig. 3.15) has four BF_4^- near its best plane,

and they are situated at the ends and the middle of the cation. Another three, also in van der Waals contact to the cation, are out of the plane and the last one is at a distance slightly longer than the van der Waals distance (3.408(10) Å).

G I. Also in G I (Fig. 3.16) four anions are situated near the best plane of a cation at the ends of the cation. At the middle of the cation, above and below the best plane, there are another four anions in van der Waals contacts to the cation.

G II. In G II one column of cations is surrounded by five columns of ClO_4^- ions forming a distorted pentagon (Fig. 3.17). *With this configuration, it is possible for the cations to be oriented in such a way that both ends and the middle of a cation (C8) are turned towards anions.* In fact there are close contacts to anions according to this, with only one exception (the contact to one end of cation B). Thus, for all cations in G II this makes contacts to three columns of anions, and of the two left in general only one has an anion in contact with the cation.

From the above results, concerning the distribution of anions around a cation, it is concluded that contacts to anions preferably are towards the ends and the middle of a cation, E or G. In G I they are somewhat to the sides at the ends, in contrast to E, where the anion is placed straight out from an end. It should be noted that the van der Waals surfaces of E and G are remarkably similar, in spite of the fact that the sulphur atoms are turned to opposite sides relative to the seven-membered ring. Thus, it seems probable that there are other factors than the shape of E and G that governs the distribution of anions around a cation. It is a fact that the heteroatoms (S) are in contact with the anions in all the structures, with only two exception in G II (to disordered anions).

Charge distribution. From calculations it is concluded that the distribution of electron density over the π -electron system is uneven (Fig. 3.11). This distribution was calculated by Yom-Tov, who in this way was able to explain the fact that electrophilic substitution occurs preferably at the β -thiophenic position. When coordinating anions, the α -position should be preferred, as it has the lower electron density.

Also at the middle of the molecule the electron density is lower, making contacts to anions more likely.

Conclusion. The observed distribution of anions around a cation is in good agreement with Yom-Tov's calculations. For all cations, there is an anion at C8 which is the most positively charged atom. The anions at the sulphur atoms are always to the side towards the carbon atom at the end of the cation, which is the α -carbon atom. The reason might be that the sulphur atoms are less positively charged than the nearest carbon atoms.

Table 3.5 The shortest distances (Å) from anions to cations. The numbers given refer to different cations as shown in Fig, 3.13 for E and Fig. 3.14 for G I. Cation number six in E is at a slightly longer distance from the anion than the other cations.

Compound E

Cation	F...S	F...C	F...H
1	3.187(13)	3.209(10)	2.45(6)
2	>4.0	3.237(7)	2.30(5)
3	>4.0	3.288(14)	2.49(5)
4	3.020(11)	3.210(12)	2.67(7)
5	>4.0	2.950(12)	2.45(7)
6	3.820(9)	3.408(10)	3.34(7)
7	3.351(11)	3.244(8)	3.20(5)
8	3.475(9)	3.082(11)	2.50(4)

Compound G I

Cation	O...S	O...C	O...H
1	>4.0	3.058(43)	2.73(16)
2	>4.0	3.364(24)	2.31(15)
3	>4.0	3.251(62)	2.58(15)
4	>4.0	3.442(18)	2.41(14)
5	3.028(25)	3.245(28)	>4.0
6	3.452(36)	3.081(33)	2.51(15)
7	3.190(25)	3.259(18)	2.73(14)
8	3.275(33)	3.094(23)	2.52(14)

Compound G II

Anion A	O...S	O...C	No of contacts
Cation			
E	3.236(36)	3.331(44)	1
B	3.187(36)	3.342(36)	1
F		3.335(39)	1
C	3.959(36)	3.455(46)	
Ref. values	3.25	3.2	2.7

Table 3.5 Continued.

ClO_4^- B Cation	O...S	O...C	No of contacts
A	3.165(28)	2.97(4)	1
B		3.256(33)	1
E		3.295(21)	1
C		3.425(36)	
D		3.278(34)	1

ClO_4^- C Cation			
D		3.232(37)	1
B		3.397(36)	
A	3.455(24)	3.233(39)	1
F	3.187(23)	3.293(38)	1
E		3.345(25)	1

ClO_4^- D Cation			
A		3.263(41)	2
B		3.317(47)	2
D	3.614(38)	3.630(50)	
E		3.355(42)	1
F	3.407(37)	3.297(39)	1

ClO_4^- E Cation	O...S	O...C	No of con- tacts	ClO_4^- F Cation	O...S	O...C	No of con- tacts
A		3.170(40)	1	A	3.512(24)	3.249(47)	1
B	3.410(24)	3.491(39)		B		3.428(42)	
C	3.254(24)	3.300(35)	2	C	3.329(36)	3.402(46)	2
D	3.408(21)	3.290(33)	1	D	3.485(35)	3.248(47)	2
E	3.199(20)	3.313(35)	1	E	3.550(31)	3.146(43)	1
F	3.406(38)	3.354(34)		F		3.365(42)	1

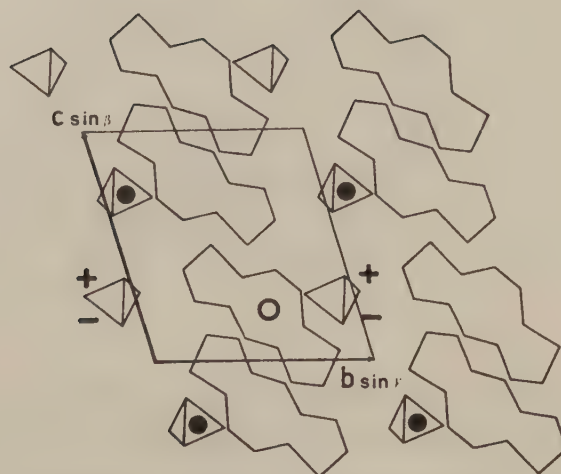


Fig. 3.15 Compound E. Coordination of BF_4^- to a cation. The central cation is marked with a small ring. Anions at the same height in the a -direction with a filled circle. Cations over and under with a + or - respectively.

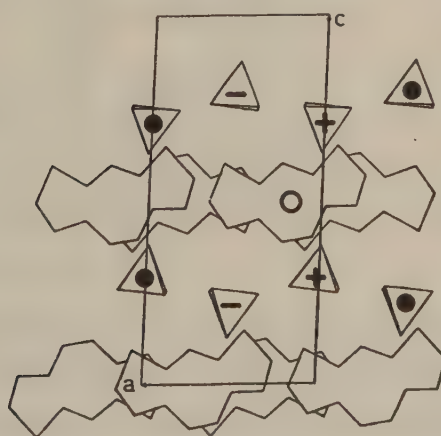


Fig. 3.16 Compound G I. Coordination of ClO_4^- ions to a cation. The central cation is marked with a small ring. Anions near the best plane of the cation are marked with a filled circle. Anions over and under the plane with a + or - respectively.

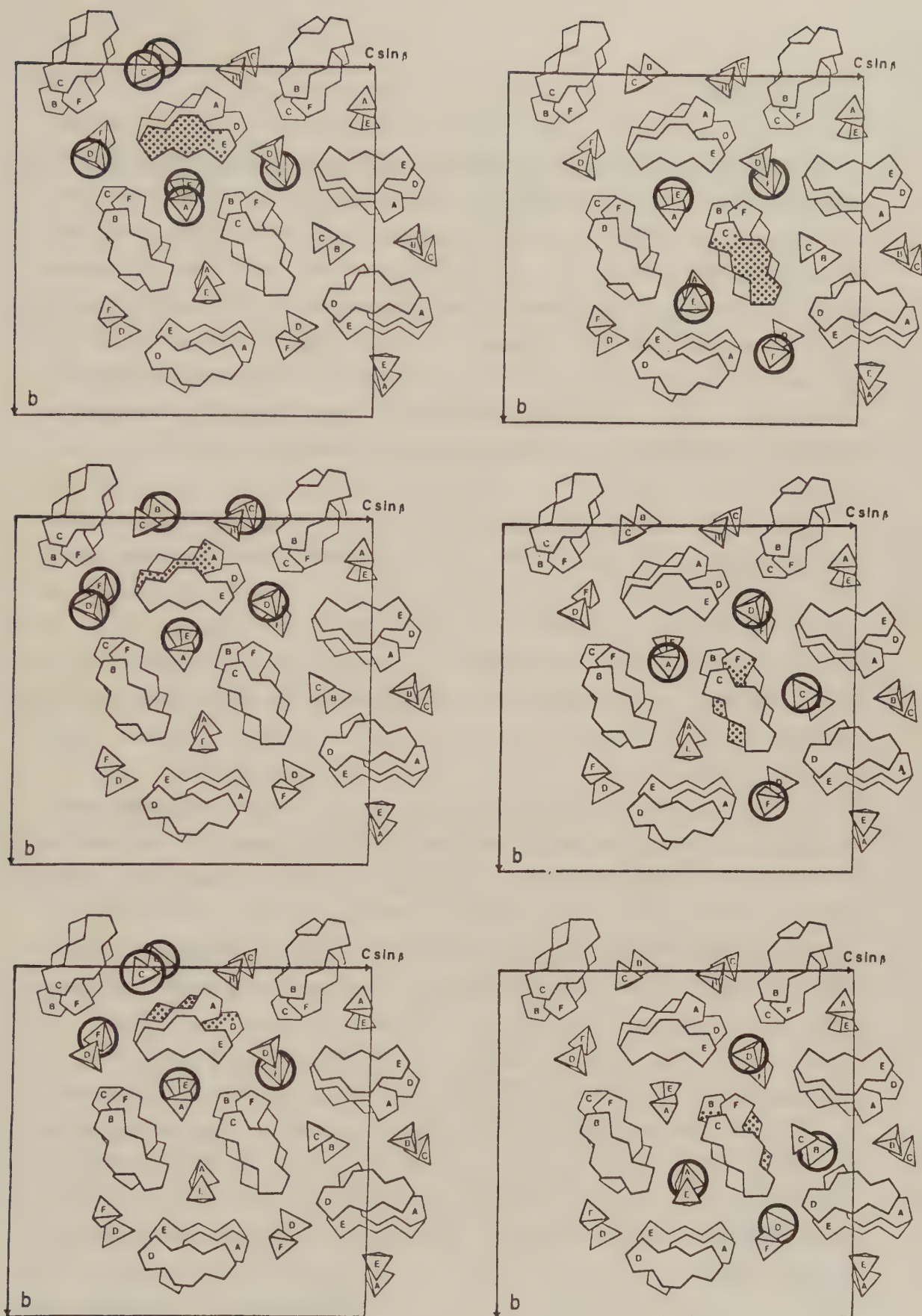


Fig. 3.17 The coordination of ClO_4^- ions to cations A, B, C, D, E and F in G II. The central cation is marked with dots and the coordinated ClO_4^- ions are encircled.

3.4 Disorder

Coordination of cations to anions. Different orientations. E. In the present structures the anions are disordered, and in E and G I there are two main orientations. In E there are very short contacts to both orientations, I and II (Fig. 3.18). The cations, which are in van der Waals contacts, are the same for both orientations. The eighth one (no. 6) is at a slightly longer distance for orientation I (3.8 Å) than for orientation II (3.4 Å) (cf. Fig. 3.13). There is one F-S contact for orientation I and two for orientation II. The latter F-S distances connect two neighbouring layers of cations (vide infra).

G I. In G I there are similarly very short contacts to both orientations (Fig. 3.20). Six cations for both orientations are in van der Waals contacts, with two cations near (cf. Fig. 3.14). The cations are numbers 1 and 3 for orientation I, and 5 and 7 for orientation II. There are two O-S contacts for orientation I and one for orientation II. The O-S distances for orientation I are connecting two different layers of cations.

G II. The anions A, D and F in G II are disordered. D and F have no short O-S distances, and A has two but to the same O atom (Fig. 3.21). The other ClO_4^- ions, which are more ordered, have at least two short contacts (O-S or O-C) to different O atoms. There are not as short O-S and O-C contacts as in E, possibly depending on temperature movement or disorder. The van der Waals contacts are in general to hydrogen atoms.

Conclusion. From the considerations above, it seems as if contacts to sulphur atoms have an important role to stabilize the anion in certain positions. There are namely fewer short contacts with increasing disorder. Of the cations surrounding an anion, there are in all the structures a few ones, which are only nearly in van der Waals contacts with an anion.

Disorder from the refinement. E. The orientations I and II occur in the proportions 0.64 to 0.36 respectively (cf. Determination and Refinement of the Structures). The orientations and the proportions of I and

II relative to each other, are somewhat different at room temperature compared to low temperature (Fig. 3.19) (cf. article E). The thermal parameters for the F atoms are larger than for the other atoms of the structure. All temperature factors are directly proportional to the absolute temperature, indicating that the disorder is not drastically changed by temperature. The residual electron density for the ions are given in Fig. 3.22. There are probably additional orientations for the BF_4^- ion, although only to a minor extent. By X-ray methods it can not be decided whether the disorder is of a dynamic or a static type. In the cation there is some electron density at the midpoint of bonds, which might be due to the bonds between atoms. These features are, in contrast, very clear in A which is also determined at low temperature (cf. article A). The more diffuse appearance of electron density for the cation in E is probably due to the influence of the BF_4^- ion on the accuracy of the determination.

G II. The values of the temperature factors are much higher for ClO_4^- ions A, D, F than for B, C, D. The residual electron density is higher than for compound E, and the highest values are found near ions A, D and F. The more ordered ions B, C and E have lower electron densities and values for the cations are comparable to these. For the cations, there are peaks mainly at the midpoint of bonds, which might be caused by rotation 180° of a fraction of the cations.

Weissenberg photographs. G II. There are areas with diffuse intensity in Weissenberg recordings of G II around b and c, indicating disorder (cf. article E). Such areas are not present in recordings around a. A recording with b as rotation axis is shown in Fig. 3.23, and it shows diffuse intensities on every third bow of h and at 2 0 4. In rotation photograms around a there are streaks originating at 0 0 0 (Fig. 3.24). Thus, when rotating around axes b and c, which are approximately in the plane of cations, diffuse intensity appear. When rotating in the direction, which is roughly normal to the planes of cations, there are not corresponding diffuse areas. In a rotation photogram, however, there are indications of disorder.

It is assumed that some disorder of cations are the cause of the diffuse bows, as there are three cations in the columns along a but

only two ClO_4^- ions. The appearance of the Weissenberg photographs are the same both at 173 and 295 K, indicating no change of disorder.

E. A close inspection of Weissenberg photographs of E, searching for similar features as in G II, was done. In a rotation photograph around a, which is normal to the cation planes, some streaks at the strong reflexions in the second zone was observed. The very strongest reflexions (2 0 0, 2 1 0, 4 1 0) in Weissenberg photographs with b and c as rotation axes have diffuse sides, which probably is an indication of disorder. Thus, although to a much lower extent, there are features also in E which indicate disorder.

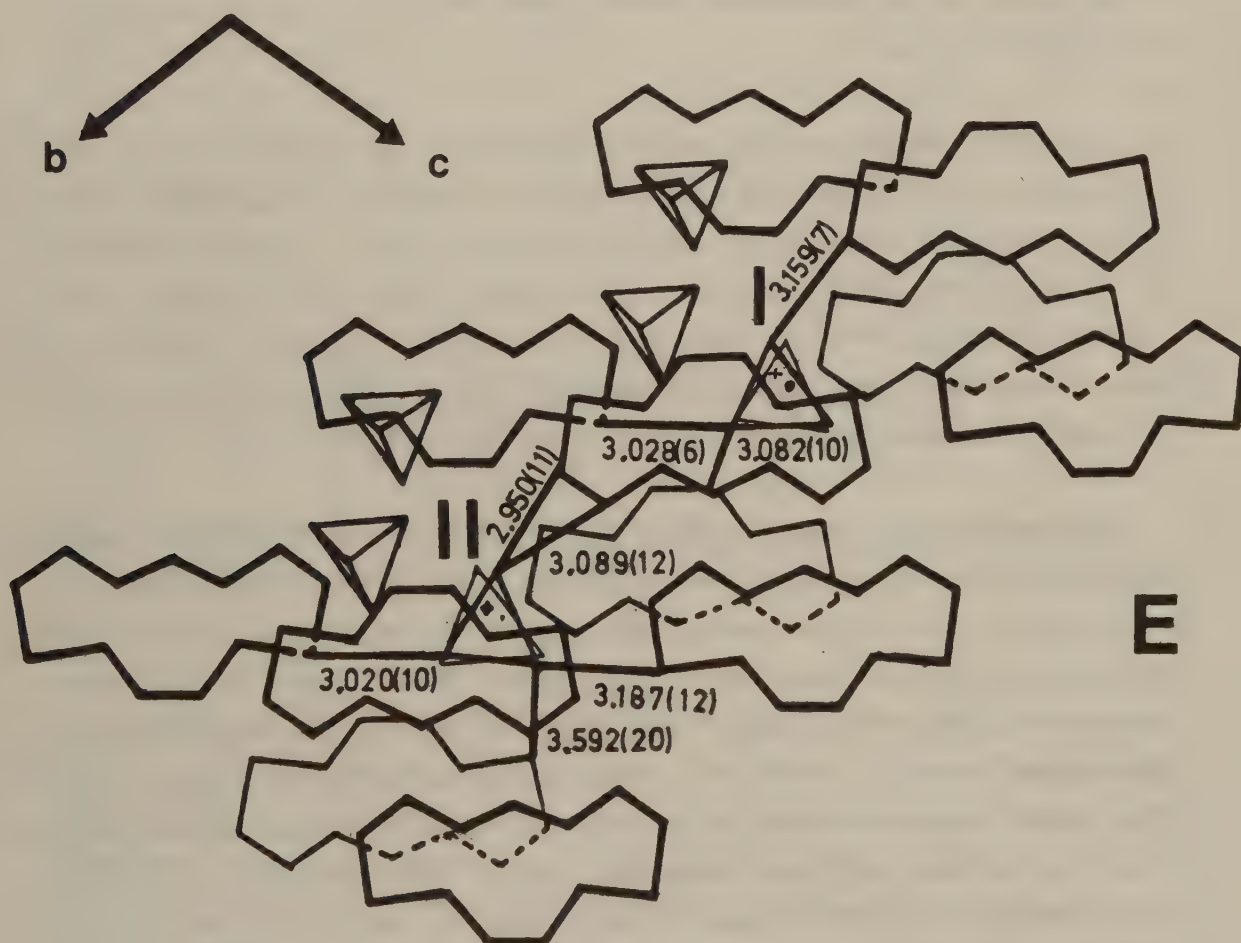


Fig. 3.18 Short distances (Å) to the BF_4^- ion in two different orientations (I and II). The figure is a projection in the direction of the normal to the best planes of cations and the directions of b and c in the projection are shown.

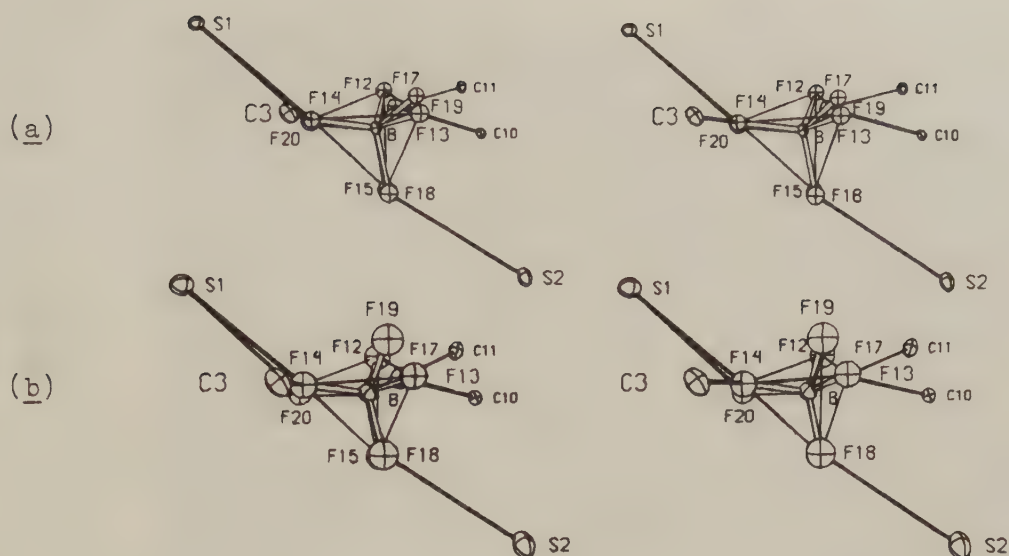


Fig. 3.19 The tetrafluoroborate ion of E at two different temperatures; (a) at 143 K and (b) at 295 K. 15 % probability ellipsoids are shown. Short contacts are given. The ion is seen from the same direction as in Fig. 3.8 (a).

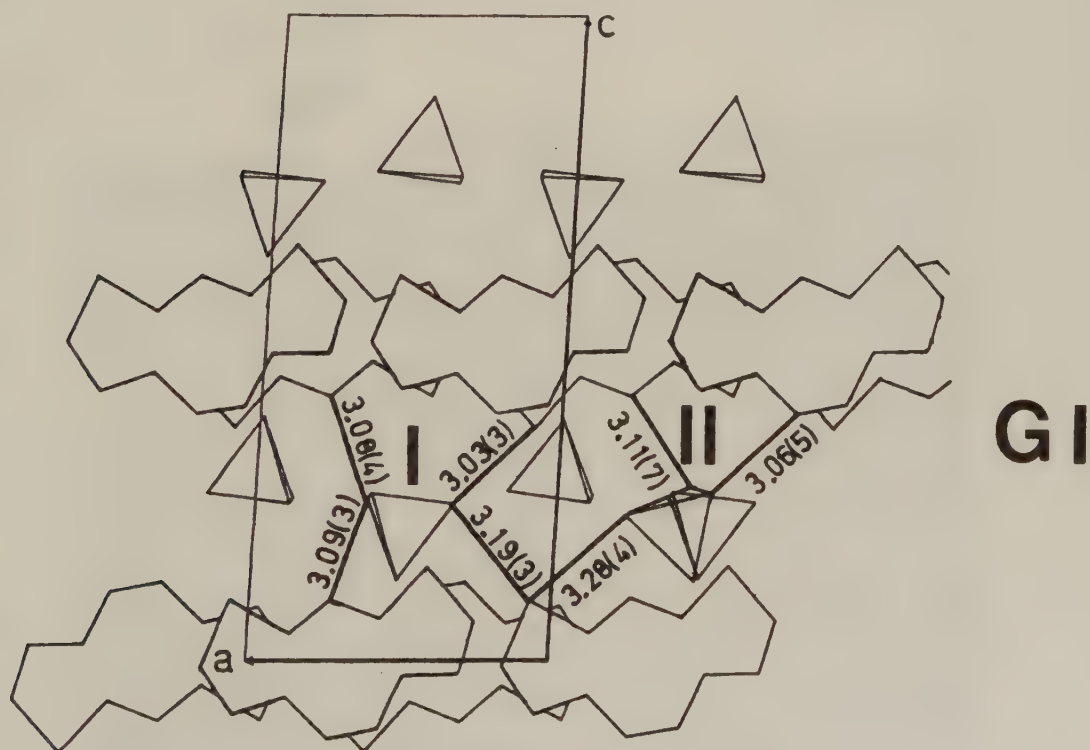
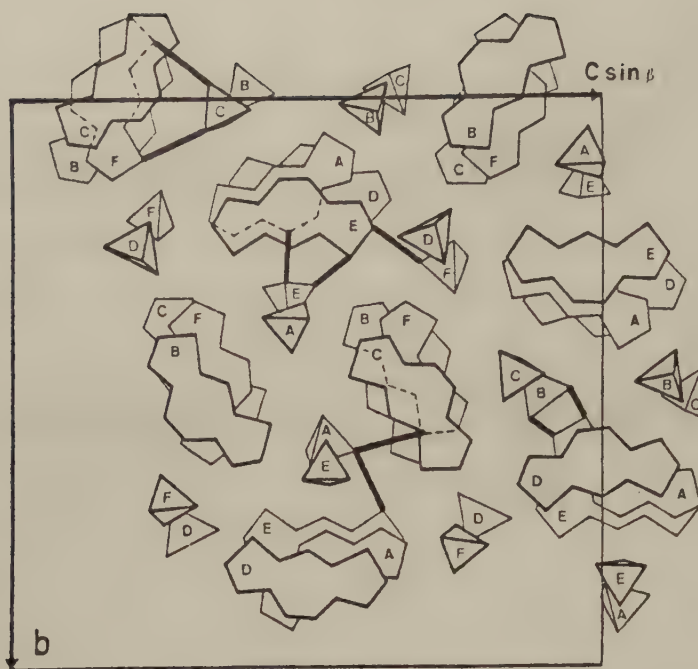


Fig. 3.20 Short distances to the ClO_4^- ion in two different orientations (I and II). The figure is a projection in the direction of b.



G II

Fig. 3.21 G II. Short distances around the ClO_4^- ions.



Fig. 3.22 The residual electron density in the vicinity of the ions E projected from a difference map. The maximum residual electron density is $0.67 \text{ e } \text{\AA}^{-3}$. Contours are drawn for 0.2, 0.4, ... and 0.4, 0.5, ... times $0.67 \text{ e } \text{\AA}^{-3}$ in the vicinity of the cation and the anion respectively. $\underline{b}$ points towards the reader. Fractional coordinates $\times 10^2$ along $\underline{b}$ for the highest peaks and for the atoms are given (143 K).

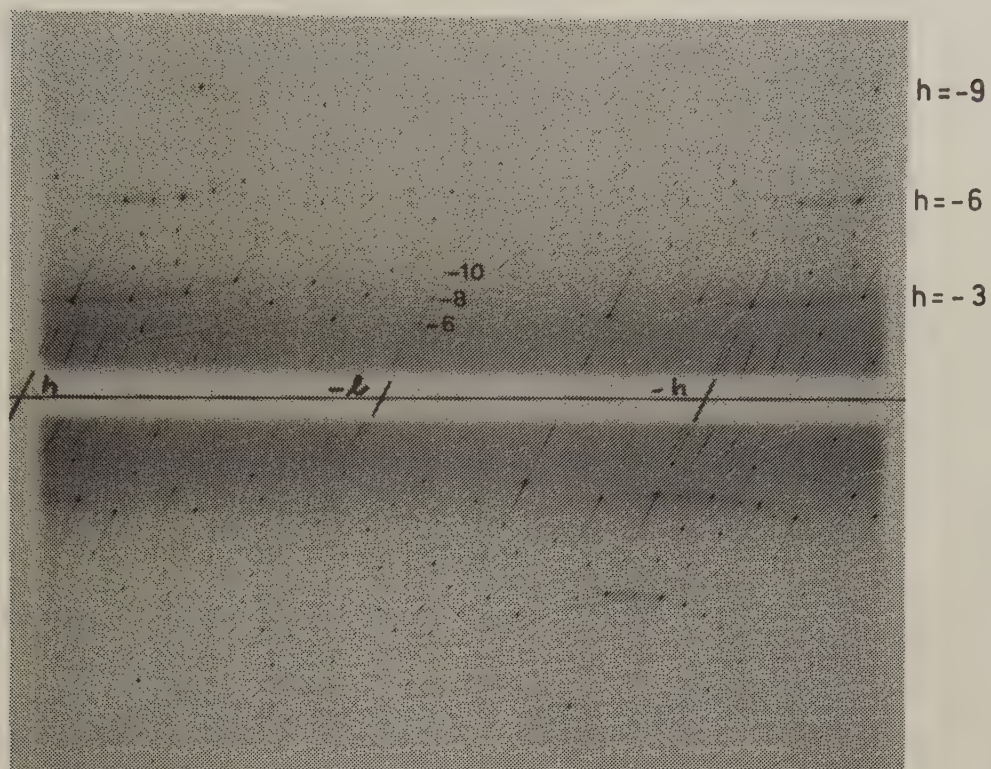


Fig. 3.23 A Weissenberg photograph of G II recorded with $\underline{b}$ as rotation axis. Only the central part is shown.

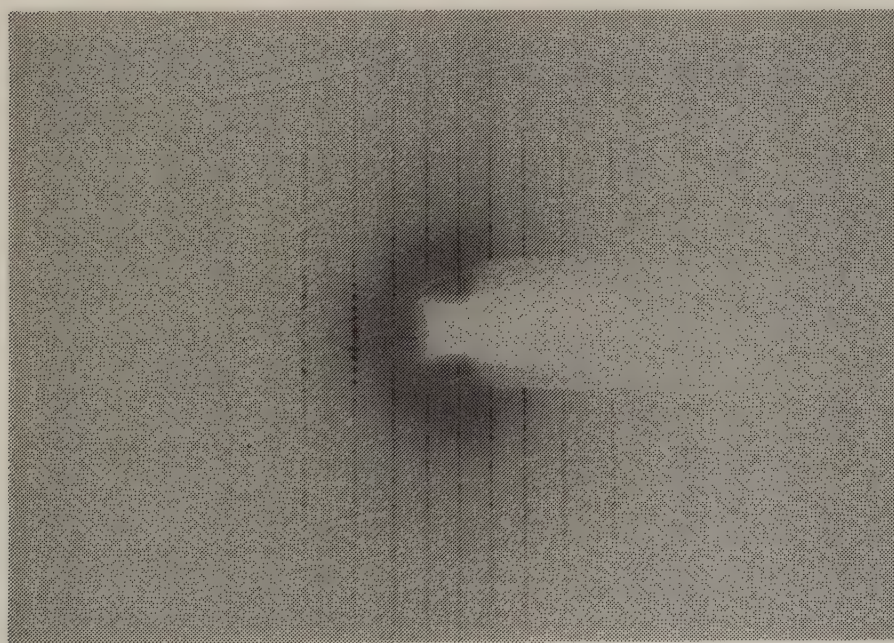


Fig. 3.24 A rotation photograph of G II recorded with $\underline{a}$ as rotation axis.

MOLECULAR STRUCTURE

4. MOLECULAR STRUCTURE

The conformations of the present molecules or cations are shown in Figs. 4.1-5. They are all remarkably similar and roughly planar. The ketone B has one single bond more in the seven-membered ring than ketone A (cf. Introduction), and takes a twisted form whereas A has a boat conformation. The cyclohepta-dithiophen-ylum (tropylium) ions (E and G) have also boat conformations, with even smaller but significant angles between the thiophene planes (Table 4.1). None of the present molecules coincide with a symmetry element of the crystal, i. e. have any inherent crystallographic symmetry. From the views of Figs. 1-5, an approximate (idealized) symmetry has been assigned to each of them, and are given in Table 4.1.

Deviations from planes. The observed conformations of the molecules deviate slightly from the idealized ones, and statistical methods have been used to decide whether these deviations are significant or not. The planarity of the ring systems have been studied by fitting best planes by least-squares to the ring atoms. The deviations of atoms from these planes are small (Table 4.2). From a statistical point of view, the deviations are significant for some of the rings, i. e. the rings are not strictly planar. Of course, a very slight deviation from planarity can only be detected in a structure determination of sufficiently high precision. The thiophene rings of B show much smaller deviations from their respective planes than the ones of the other molecules, and are both strictly planar. The atoms of the central ring, which are close to a thiophene ring, often deviate from the respective thiophene plane. This is especially pronounced for B and indicates a distortion from the idealized symmetry.

Distortions. The distortions of the present molecule from their idealized symmetry can also be seen in Fig. 4.6. In B the deviation of C(8) from the thiophene plane I is quite large, as mentioned above (0.12 Å). A has a minor twist of the whole molecule lengthwise. Thus, the boat conformation of the central ring is distorted by a twist. In contrast to A, one thiophene ring (II) is planar in E and there is a twist only of rings I and III. The cations G are encountered in two polymorphs, G I and G II, and moreover in the latter one in six differ-

rent positions. However, due to disorder the precision of the determinations are not high enough to ascertain the significance of the small deviations from planes (Table 4.2).

Bond lengths and angles. Precision and accuracy. The conformations can be studied also by comparing corresponding bond distances and angles within a molecule (cf. articles). The differences between corresponding bond lengths of the left and right sides of a molecule are small for the present substances. From normal probability plots (Hamilton, 1974), it was concluded that the differences are not significant for A and that for the other compounds there are generally small systematic deviations (Table 4.3). The e.s.d.'s of the bond lengths and angles are generally overestimated for the low temperature determinations.

Discussion of deviations from idealized symmetry. The question arises whether the small deviations from idealized symmetry, discussed above, are actual properties of molecules in the crystals or whether they are artefacts caused by experimental systematic errors. From a chemical point of view there is no reason for asymmetry, and molecules unaffected of other ones (e. g. in the gaseous state) should exhibit the idealized symmetry.

Crystalline forces. Molecules are in crystals affected by crystalline forces. Kitaigorodsky (1973) stated that the crystalline field does not change bond lengths and angles of organic molecules, as the influence from the crystalline field is very small compared to what is needed to alter bond lengths or angles. However, rotation around a single bond might be possible.

In the present molecules and ions there is generally a very small twist, as discussed above. The influence on a molecule with idealized symmetry, which is needed to effectuate such a twist, is probably small. To perform it, just slight torsion of bonds is needed. However, the twist observed might also be caused by some systematic error, and this matter cannot be decided. In B there is one very large deviation, which might be ascribed to systematic errors. In this context, it might be noted that a correction for anomalous dispersion could not be made for this compound.

Steric interactions. There is also the possibility of steric interactions within molecules, which might distort the idealized symmetry. Steric interactions in the present molecules are small (cf. intramolecular interactions, p. 81). I. e. the distance between the H atoms of the central ring (C(2)-C(3)) could be increased by a twist. However, there is no indication that the H atoms mentioned are bent out of plane accordingly.

Temperature movement. Beside the twist, another systematic effect indicated by measured values is the difference between corresponding bond lengths of the left and right sides of a molecule. It seems to be larger at room temperature than at low temperature, indicating influence from temperature movements. Another point is that, with a few exceptions, the bond distances of E determined at 295 K are smaller than the ones determined at 143 K. This is probably an apparent shortening due to thermal motion. *It is likely that the systematic effects mentioned above are at least partly caused by disorder of molecules or ions, as it is known that some of the structures are disordered.*

Table 4.1 Conformations of molecules and cations. C_2 is the notation for rotation symmetry and σ for mirror plane.

Compound	Conformation of seven-membered ring	Angle between thiophene planes I and II	Approximate (idealized) symmetry	Direction of symmetry element
B	twisted	158.2(3) ^o	C_2	Two-fold rotation axis through C(8) and the midpoint C(2)-C(3)
A	twisted-boat	171.6(8)	σ	Mirror plane at right angle to the best plane and passing through C(8) and the midpoint C(2)-C(3).
E	twisted-boat	175.3(4)	σ	
G I	twisted-boat	177.7(4)	σ	
G II				
A		178.6(12)		
B		178.1(14)		
C		178.7(13)		
D		179.1(10)		
E		176.9(8)		
F		174.8(27)		
mean		178(2)	σ	

Table 4.2 Deviations of atoms from planes. The maximum deviations of atoms from their best planes are given. They are marked with an asterisk if the atoms of the respective plane, from a statistical point of view, do not strictly form a plane. I denotes the best plane of the atoms of the S(1) thiophene ring, II correspondingly the S(2) thiophene ring, III the central ring and IV the whole molecule (cf. Fig. 4.7).

Compound	Maximum deviations from planes ($\times 10^3$ Å)						E.s.d.'s of C atoms $10^3 \times \sigma_c$	Temp. K
	Atoms within rings				Neighbouring atoms to rings			
	I	II	III	IV	I	II		
B	5	4			23 ^x	124 ^x	7	295
A	10 ^x	12 ^x	61 ^x	172 ^x	37 ^x	45 ^x	5	173
E 143 K	13 ^x	2	31 ^x	76 ^x	84 ^x	7	5	143
295 K	11	7	24 ^x	79 ^x	73 ^x	16	9	295
Wb 295 K							30	295
G I	6	10	15	36 ^x	69 ^x	36	13	295
G II							32	173
A	28	37	45	55	32	122 ^x		
B	42	29	28	57	35	27		
C	45	23	33	70	77	86		
D	27	17	28	54	32	107 ^x		
E	14	9	57	70	14	8		
F	13	33	66 ^x	97	13	33		

Table 4.3 Comparison of bond lengths related by the idealized symmetry. Bond distances (bonded plus non-bonded) are compared between the left and right sides of a molecule (or ion) by normal probability plots (Hamilton, 1974).

The values of slope and systematic differences obtained by the plot can be used to evaluate the e.s.d's of bond lengths. E. g. for A, the e.s.d's are overestimated and should be multiplied by a factor of 0.7. When there is a systematic difference, a factor obtained by adding the absolute values of slope and systematic difference ($|k| + |l|$) has been used.

Compound	Slope of line k	Systematic differences l	Sum of absolute values $ k + l $
B	1.1	-0.7	1.8
A	0.7	-0.1	0.8
E 143 K	0.7	0.7	1.4
295 K	1.3	0.9	2.2
Wb 295 K	2.2	0.2	2.4
G I	1.2	-0.7	1.9
G II			
A	1.0	-0.45	1.45
B	0.6	0.4	1.0
C	0.7	0.5	1.2
D	1.0	0	1.0
E	1.5	-0.3	1.8
F	0.5	0	0.5

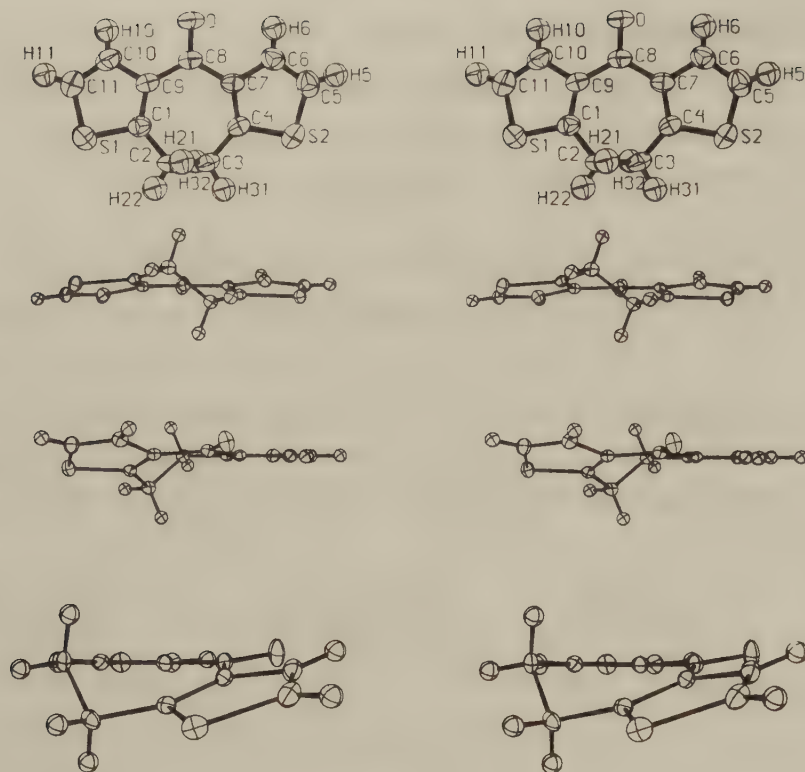


Fig. 4.1 A stereoview of one molecule of B viewed from four different directions. 50 % probability ellipsoids are shown in the upper-most figure. An approximate two-fold rotation axis passes through C(8) and the midpoint of the C(2)-C(3) bond.

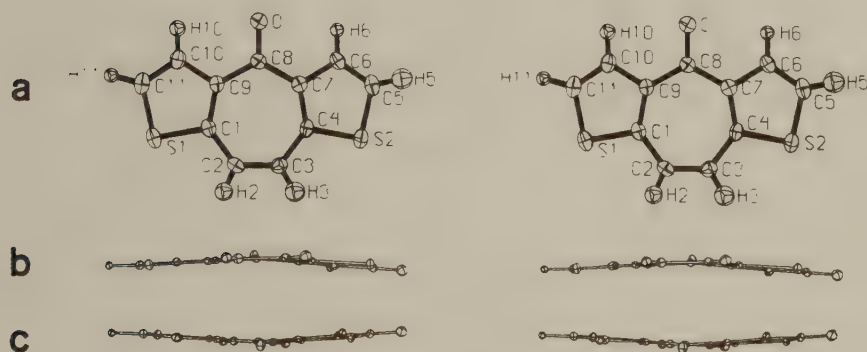


Fig. 4.2 A stereoview of molecule A from three different directions. In (a) 50 % probability ellipsoids are shown, in (b) C(2) and C(3) point towards the reader and in (c) O points towards the reader. An approximate mirror plane is directed at right angle to the best plane of the ion and passes through C(8) and the midpoint of the C(2)-C(3) bond.

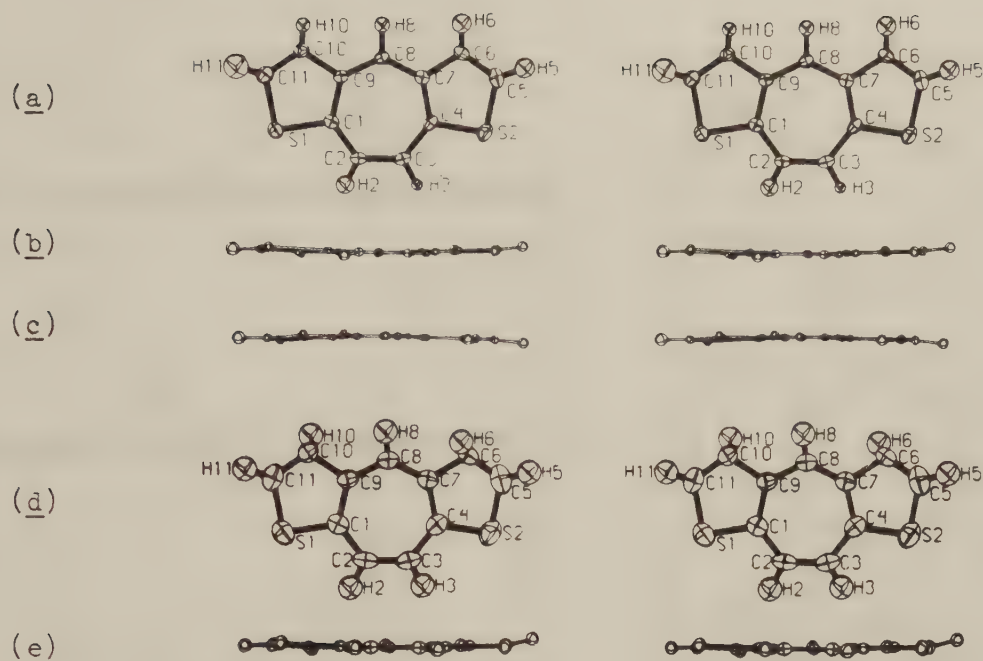


Fig. 4.3 A view of the cation E from three different directions and at two different temperatures; (a), (b), (c) at 143 K and (d), (e) at 295 K. In (a) and (d) 50 % probability ellipsoids are shown, in (b) and (e) C(2) and C(3) point towards the reader and in (c) C(8) points towards the reader. There is an approximate mirror plane oriented in the same way as for molecule A.



Fig. 4.4 A view of one molecule of G II. 50 % probability ellipsoids are shown. The molecule is oriented in the same way as in Fig. 4.7 (d). There is a mirror plane in a corresponding way as for molecule A.

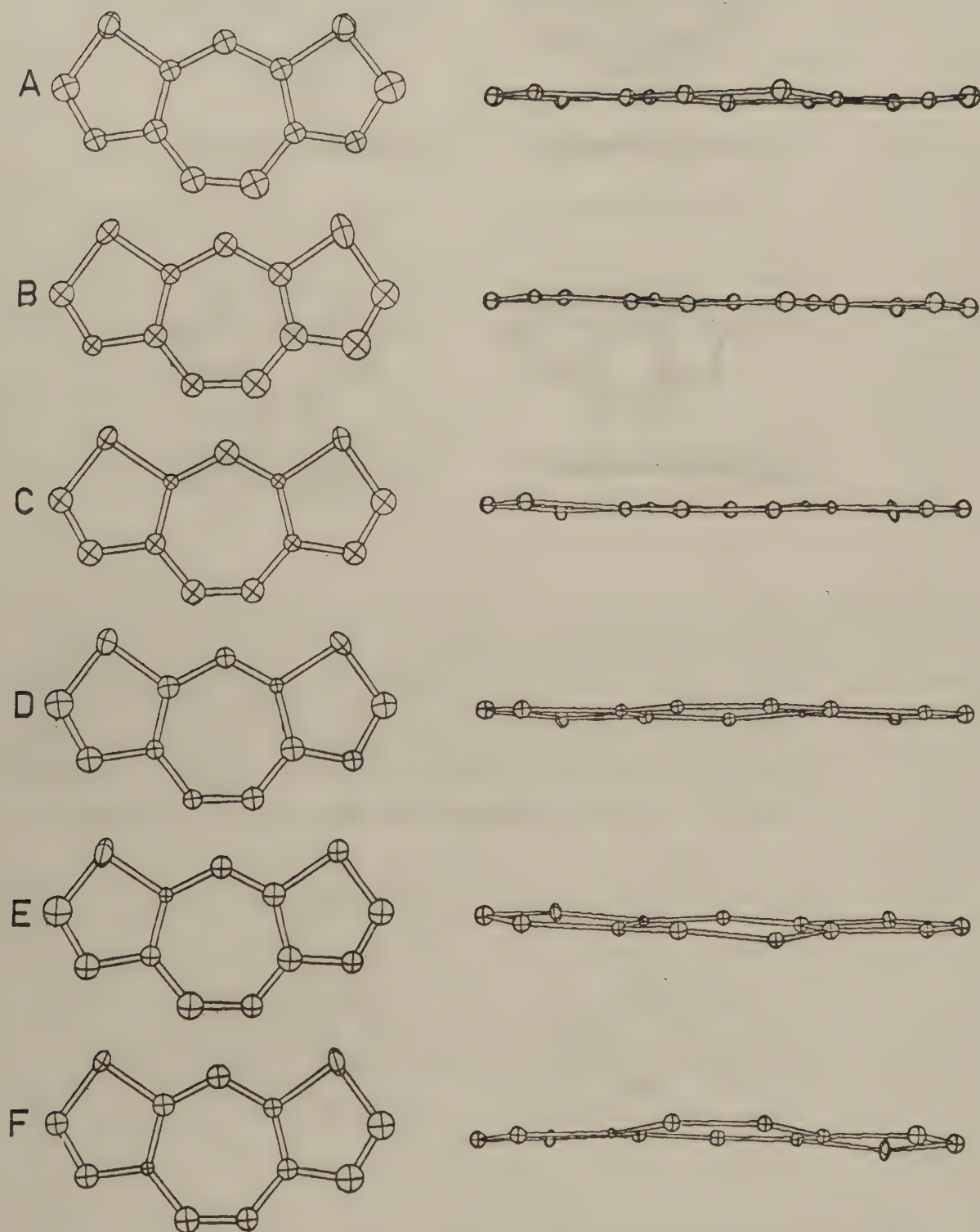


Fig. 4.5 A view of the six molecules of G II. On the right side they are seen with the C(2)-C(3) bond pointing approximately towards the reader. Notations of atoms are as in Fig. 4.7 (d).

Mean values. Assuming the idealized symmetry, mean values of bond distances and angles can be calculated and are given in Fig. 4.7. To be able to compare bond distances from structure determinations of both high and low precision, the e.s.d.'s have been multiplied by a factor related to the precision and accuracy of the structure determination in question (Table 4.3).

Relative bond lengths. As mean values of bond lengths are used (Fig. 4.7, Table 4.4), only notations of the left half of molecules will be used when referring to bonds. The S-C bond to the central ring (S(1)-C(1)) is longer than the outer S-C bond (S(1)-C(11)) in the compounds, however, the difference being significant only for A. In molecule B, the formal double bond of the central ring (C(1)-C(9)) is probably longer than the thiophenic one. The formal single bonds of the central ring are all longer than the thiophenic single bond (C(9)-C(10)). For A, similarly, the central double bond (C(1)-C(9)) is longer than the thiophenic one (C(10)-C(11)) and the central one (C(2)-C(3)), which here is a double bond in contrast to compound B. The formal single bond of the central ring (C(8)-C(9)) is longer than the other single bonds, which are remarkably short. Thus, for A and B, there are large relative differences between single and double bonds, as given by their structure formulae.

In the cations E and G II, the bond length interval of the central ring is much smaller than for A and B. Here, there is no short double bond or long single bond, and the formal single bonds are even shorter than for A and B. One of the formal double bonds are even longer than the formal single bonds. The thiophenic bonds are of about the same length as in A and B, and represent a larger bond length interval than the bonds of the central ring.

Bond alternation. A general feature observed when examining the series of compounds going from B to G II, is that the bond distances of the seven-membered ring approach each other and the values of bond lengths in benzene and graphite (Fig. 4.8, Table 4.4). From ketone A to ion E there are even relative changes, so that the longest bond now is the annealed double bond (C(1)-C(9)), as mentioned above.

In the thiophene rings there are no such drastical change in bond lengths; the fused double bond (C(1)-C(9)) is not considered here. For the C-C bonds the largest change in the single bond (C(9)-C(10)) is from A to E, and for the double bond from E to G II (probably significant). The length of the S-C bonds seem to increase slightly from E to G II, but this increase is not significant.

Conjugation. The general approach of bond lengths indicate that, for the seven-membered ring, the conjugation of single and double bonds increases from B to G II of the series. For the thiophene rings, in contrast, there is no change in conjugation (rather a decrease than an increase).

Degree of aromaticity. A numerical value of the conjugation or degree of aromaticity can be given by an aromaticity index. This index has the value 1 for a molecule with all single and double bonds equal to the value for benzene, and 0 for a molecule with quite separated single and double bonds (Table 4.5). *The aromaticity index for the central ring increases from B to G II, as expected from the bond lengths discussed above. For the thiophene rings it increases from B to A and from E to G II. In contrast to the index for the central ring, there is not a continuous increase, but instead the index is lower for E than for A. The fused bond (C(1)-C(9)) is included here. The increase of aromaticity in the series is in accordance with the resonance structures of the molecules and ions, as well as with chemical reactivity as discussed in the introduction.*

C-O distance. For the ketone, also the length of the carbonyl bond (C-O) can be used to estimate the aromatic character of molecules. The C-O bond and the (C(1)-C(9)) bond is shorter for B than for A, in good agreement with the C-O stretching frequencies. *This fact indicates less delocalization for B than for A.*

Angles between thiophene planes. An important factor in the context of aromatic character or bond delocalization is the planarity of molecules. As already shown (Table 4.1), the angles between thiophene planes I and II go towards 180° in the series from B to G II, *which parallels an increase in conjugation of the seven-membered ring (cf. Table 4.5).*

E. g. a boat form of the seven-membered ring must have torsion in the bonds, giving a smaller overlap of p-orbitals than a planar form. The twist in bonds (torsion) is small for the present compounds, except for B (Table 4.6).

Angular strain. In the seven-membered ring of the two ketones B and A, the angle at the carbonyl bond (C(7)-C(8)-C(9)) is $122.5(4)^\circ$, and the average value of the other angles in the central ring is 129.5° (Table 4.7). These values should be compared to those for sp^2 -hybridization, 120° , and for a heptagon, 128.6° . Assuming sp^2 -hybridization, it is clear that there is angular strain in the seven-membered ring, and to about the same extent for the two compounds mentioned. The angle at the (C(2)-C(3)) single bond in B is $112.0(5)^\circ$, which is larger than the tetrahedral value, 109.5° . For the ions E and G II, the angle (C(7)-C(8)-C(9)) is larger (for E $129.1(4)^\circ$), and the angular strain is probably about the same as for B and A.

Angles. The angles at the thiophene rings (C(3)-C(4)-C(7) and C(4)-C(7)-C(8)) are smaller for E than for A, and the angle at the S atom is always the largest of the two ones. There are also small differences for the angles in the thiophene rings.

Conclusion. The angular strain of the seven-membered ring for the present compounds, would be much less in a hypothetical boat form. Therefore, considering angular strain in a seven-membered ring only, it would be advantageous with a boat form instead of a more planar form, as for the series B to G II. The fact that the actual molecules are nearly planar indicate that the effects of conjugation (delocalization of electrons) dominate over that of angular strain. The angle between the thiophene planes is indicative for the extent of conjugation, i. e. the more planar a molecule the higher degree of aromaticity.

Intramolecular interactions. Another factor which influences the conformation is intramolecular interactions. They are between non-bonded atoms within a molecule, mainly the peri atoms of the central ring and the annelated rings (Fig. 4.9). The molecules of the present series are roughly planar, and by taking a boat form the interactions mentioned would be diminished. As this structure does not occur, the interactions

are not large for the present series B to G II. The relevant distances are compared in Fig. 4.9. to the van der Waals distances observed between molecules (intermolecular distances), and intramolecular van der Waals distances, given by Bartell (1960). For the series the distances are in general long relative to the distances given by Bartell, indicating small interactions.

It is concluded that for the present thiophene compounds a high tendency towards aromaticity keeps the molecules planar against the influence from angular strain and intramolecular interactions.

Table 4.4 Mean values of bond distances (Å). The e.s.d.'s for E, A and B are multiplied by 1.7, 0.7 and 1.6, respectively (see text).
Notation: s = single bond, d = double bond. The reference distances are taken from International Tables for X-ray Crystallography (1962) and from Kitaigorodsky (1973).

Seven-membered ring

	C(2)-C(3)	C(1)-C(9)	C(1)-C(2)	C(8)-C(9)
Compound	d or s	d	s	s
G II (173 K)	1.40(3)	1.432(12)	1.417(13)	1.403(12)
E (143 K)	1.378(5)	1.435(7)	1.409(7)	1.399(7)
A (173 K)	1.352(4)	1.393(3)	1.425(3)	1.467(3)
B (295 K)	1.516(12)	1.373(7)	1.493(8)	1.479(7)
Reference bonds	Double (simple)	Aromatic	Graphite	Single (partial)
	1.337(6)	1.395(3)	1.4210(1)	1.476
	Single (partial)			
	1.507			

Thiophene rings

	C(10)-C(11)	C(9)-C(10)
Compound	d	s
G II (173 K)	1.373(13) [C(10)-C(11)]	1.441(13) [C(1)-C(11)]
E (143 K)	1.344(8)	1.452(7)
A (173 K)	1.345(4)	1.426(4)
B (295 K)	1.340(8)	1.430(8)
	S(1)-C(1)	S(1)-C(11)
Compound	s	s
G II (173 K)	1.742(9) [S(1)-C(9)]	1.730(10) [S(1)-C(10)]
E (143 K)	1.729(5)	1.723(5)
A (173 K)	1.738(3)	1.716(3)
B (295 K)	1.722(6)	1.714(7)
		C-O
		1.240(3)
		1.215(8)

Table 4.5 Aromaticity index according to Julg et al. (1967).

The index is given by $A = 1 - k \sum_{i=1}^n (l_i - \bar{l})^2 / n \bar{l}^2$, where $k=337$ is used, $\bar{l}$ is the mean bond length, l_i is the length of bond i and n is the number of bonds in the ring. The index is calculated for the C-C bonds of the thiophene rings I and II, for the seven-membered ring III and for the whole molecule IV. Column I+II gives the index for all C-C bonds in rings I and II, and column I+II-III includes the bonds of rings I and II except the bonds in common with ring III.

Compound	I	III	II	I+II	IV	I+II-III
B	0.69	0.52	0.81	0.69	0.35	0.63
A	0.78	0.74	0.81	0.81	0.70	0.71
E	0.71	0.95	0.45	0.61	0.68	0.49
G I	0.72	0.98	0.69	0.74	0.85	0.52
G II (A-F)	-	0.97	-	0.85	0.95	0.80

Table 4.6 Torsion angles in the seven-membered ring. Mean values ($^{\circ}$) are given assuming ideal symmetry. Significant differences due to a minor twist (distortion) are ignored. For comparison the angle ($^{\circ}$) between planes I and II are also given. Notations are as in Fig. 4.7.

Compound	Double bonds		Single bonds		Angle between planes, I $\wedge$ II
	C(2)-C(3)	C(1)-C(9)	C(1)-C(2)	C(8)-C(9)	
B	70.9(6) (single b.)	3.5(7)	12.6(7)	46.1(6)	158.2(3)
A	2.2(8)	2.4(9)	5.0(7)	8.0(6)	171.6(8)
E	1.2(7)	2.6(6)	3.8(9)	1.3(5)	175.3(4)

Table 4.7 Angular strain. The top angle ($^{\circ}$) in the seven-membered ring and the average value of the other angles in the central ring are given as well as some reference values.

Reference values: sp^2 120, sp^3 109.5, heptagon 128.6, pentagon 108.0.

Compound	Seven-membered ring		Angle between planes I and II	Configuration
	Top angle C(7)-C(8)-C(9)	Average value of the other angles		
B	122.5(4)	129.5	158.2(3)	twisted
A	122.5(4)	129.5	171.6(8)	twisted-boat
E	129.1(4)	128.5	175.3(4)	twisted-boat
G II	124.5(17)	129.1	178(2)	

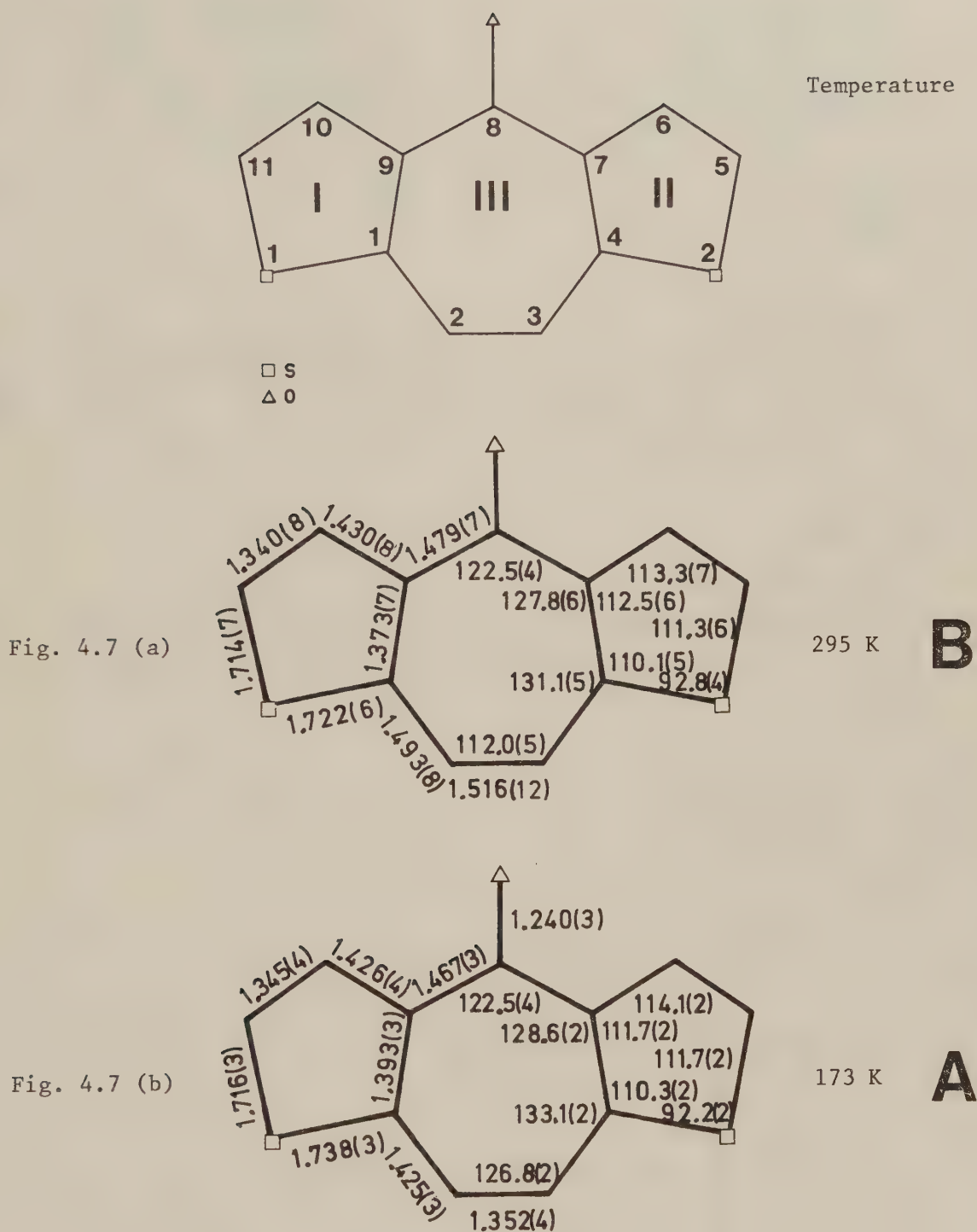
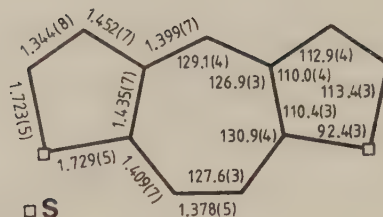


Fig. 4.7 (a), (b) Mean values of bond lengths (Å) and angles ($^{\circ}$). For each compound the e.s.d.'s of bond lengths and angles have been multiplied by a factor, which is evaluated by normal probability plots (cf. Table 4.3). The factor used is 1.6 for B and 0.7 for A. The numbering of the ring systems are presented. The e.s.d.'s are given in parentheses.



□ S

Fig. 4.7 (c)



□ S

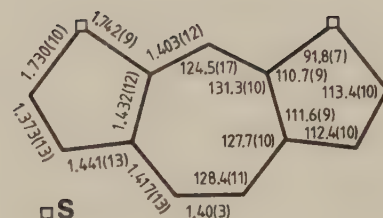
Temp.

143 K

E

□ S

Fig. 4.7 (d)



□ S

173 K

GII

Fig. 4.7 (c), (d) Mean values of bond lengths (Å) and angles ($^{\circ}$). The factor used is 1.7 for E and 1.0 for G II, cf. p. 87.

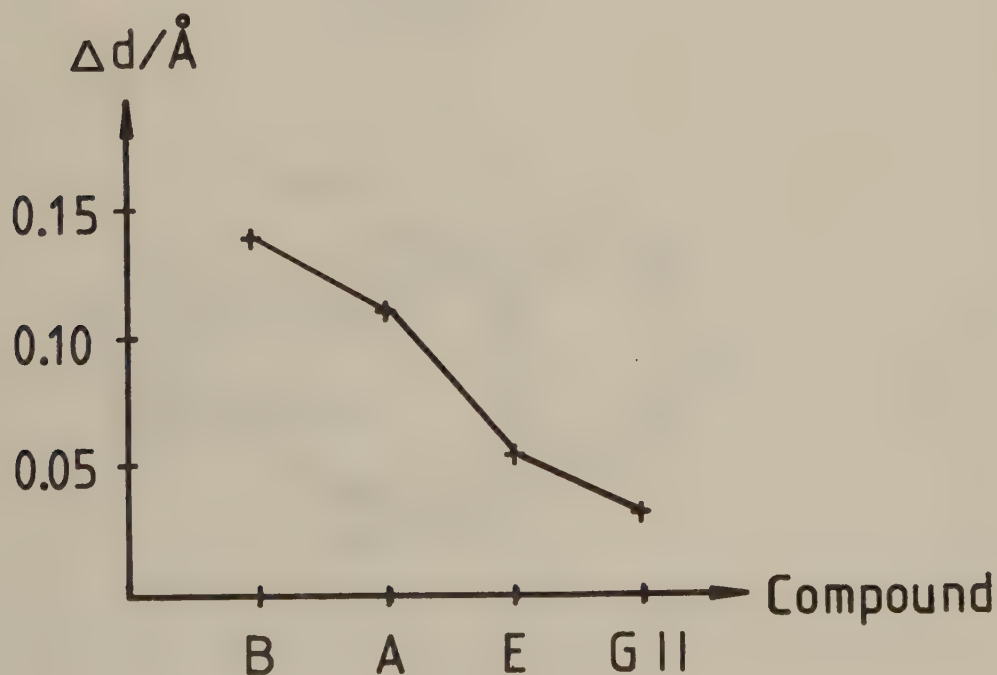
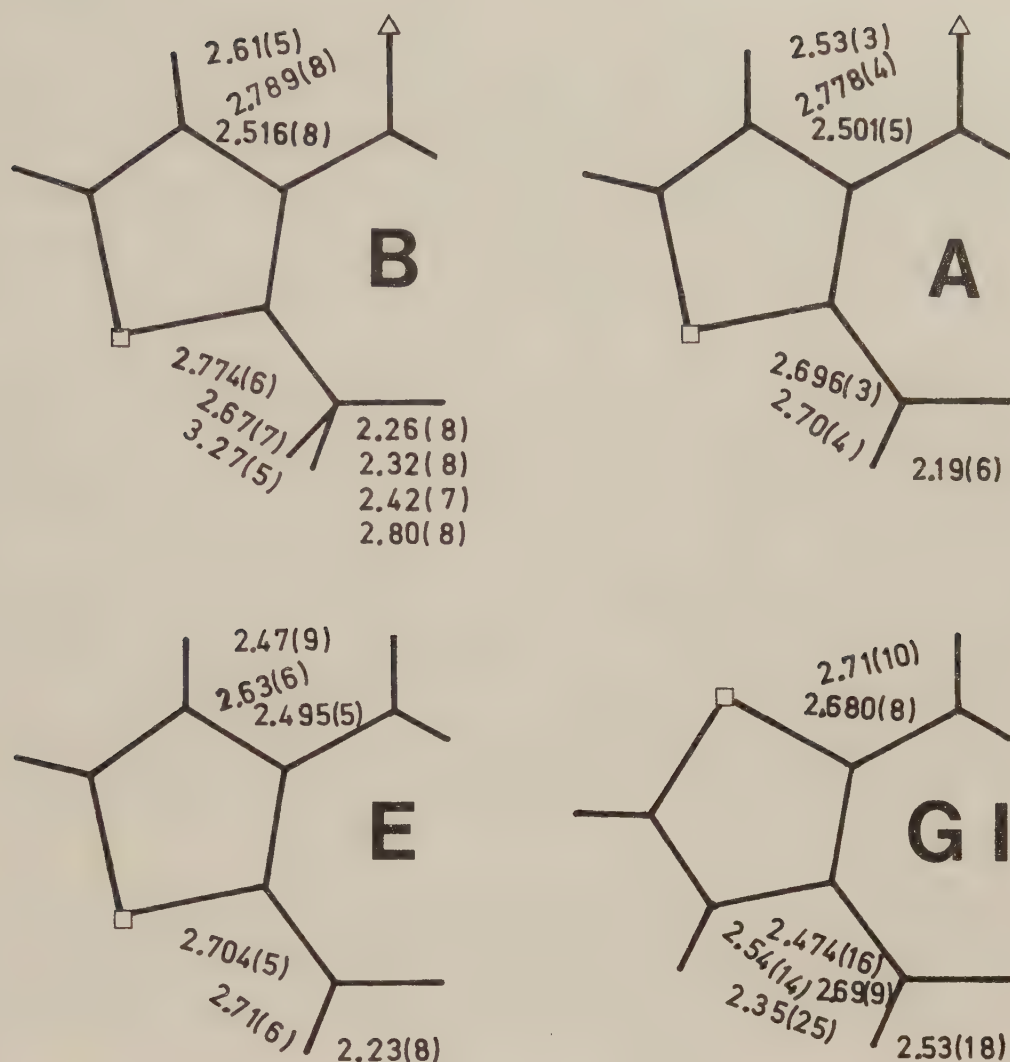


Fig. 4.8 The maximum difference (Δd) between bond distances in the seven-membered ring is plotted for each compound. $\Delta d = (d_{\max} - d_{\min})$ in ring III.



Van der Waals distances	S-C	S-H	O-O	O-C	O-H	C-C	C-H	H-H
Intermolecular, Bondi	3.45	2.95	3.0	3.2	2.7	3.4	2.9	2.4
Intramolecular, Bartell	-	-	2.26	2.38	2.05	2.50	2.17	1.84

Fig. 4.9 Intramolecular interactions. Mean values of the shortest intramolecular distances (Å) for the peri atoms are given. Reference values are van der Waals distances (Bondi, 1964), and intramolecular van der Waals distances according to Bartell (1960). These are obtained as the distance between atoms X in ethylenic molecules $H_2C = X_2$, where X atoms are supposed to be in contact with each other. For the actual shortest intermolecular distances cf. Table 3.2.

5. SUMMARY

The crystal structures of some molecular and ionic cycloheptadithiophene compounds have been determined. They form a series of increasing aromatic character. The ionic compounds are composed of large planar cations and smaller anions. They have layer or columnar structures with cations, which characteristical are parallel to each other.

It has been shown that one of the compounds has a metastable and a stable phase. The metastable one has a large complex unit cell with a columnar arrangement, in contrast to the stable one which has a small unit cell of high simplicity. The anions and cations of the metastable phase are disordered. The stable phase has a higher packing density and a much less extent of disorder, only the anions are disordered. The disorder of cations in the large unit cell have been studied. Although there is a great difference between the polymorphs, they are built up of largely parallel cations and anions, and it has been shown that a transformation in the solid state occurs.

The anions can readily be exchanged to other anions of similar size. The exchange is along columns or in planes of anions. The structural arrangement of layers and columns makes the exchange possible.

Morphology and optical properties are in agreement with the structure for the metastable phase. The refractive indices in the plane of cations are large due to the planar cations, which are all in the same direction. The relation between optical properties and structure is not so obvious for the stable phase, where there are two different directions of parallel cations.

The cations are surrounded by anions in a way that is in accordance with the theoretically calculated charge density for a cation.

The detailed conformations of the molecules have been determined to a high precision by low-temperature measurements. The molecules are approximately planar, which is a fact that could not definitely be decided by chemical means only. There are small distortions from the ideal symmetry of free molecules.

The bond lengths show an approach to each other when going from the least to the most aromatic of the compounds. The bonds are conjugated and an aromaticity index has been calculated. The index is in accordance with chemical and spectroscopic observations. The aromatic systems have a tendency to stay planar, and the influence from angular strain and H-H intramolecular interactions are not strong enough to cause more than a minor bend (towards a boat form) of molecules.

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The English text in some of the papers have been revised by Dr Bob Carter. Mr Lars Seiron has made photographic reproductions in a skilful way. Ms Helén Ingesson did the typing of the manuscript carefully.

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Acta Cryst. (1975). B31, 1396

X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems. III.* The Crystal Structure of 8,9-Dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophene-4-one

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8,9-Dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophene-4-one, $C_{11}H_8OS_2$, is orthorhombic, space group $Pn2_1a$, with $a=15.1520$, $b=4.6668$, $c=14.2083$ Å, $Z=4$. The structure was refined to an R of 0.037 for 1043 non-zero counter reflexions. The central seven-membered ring deviates considerably from planarity and the planes of the two thiophene rings form an angle of $158(2)^\circ$. The ring angles of the sp^3 carbon atoms are larger than the tetrahedral value.

Introduction

8,9-Dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophene-4-one [denoted (I) in Fig. 1] is a tricyclic system with two thiophene rings connected to a seven-membered ring containing one carbonyl group. The compound was first synthesized by Yom-Tov & Gronowitz (1973), who used it as an intermediate for the synthesis of the dithienotropylium cation (II) and of tricyclic psychoactive drugs. In order to compare the delocalization in some tricyclic systems, Gronowitz, Yom-Tov & Michael (1973) have given a comparison between the C=O stretching frequencies of saturated and unsaturated ketones, including the present saturated ketone.

X-ray investigations of compounds similar to the present one have previously been made. Thus the structures of an unsaturated dithienotropylium cation (III) (Aurivillius, 1974*a*) and an unsaturated dithienoborepinyl ether (IV) (Aurivillius, 1974*b*) have been reported. These compounds exhibit planar or nearly planar ring systems with extended π -electron delocalization. The present compound has one double bond less in the central seven-membered ring, and a lower degree of delocalization might be expected. The crystal structure of a saturated dibenzo-annelated compound (V) has been determined (Larsson, 1970) and the central ring of this molecule is found to take a deep boat form. The present investigation was started in order to compare the configurations of molecules of saturated and unsaturated cycloheptadithiophene compounds.

X-ray diffraction work

A specimen was kindly supplied by Dr B. Yom-Tov. The single crystal used for the diffractometer work was a colourless needle of length 0.2 mm in the direction of **b** and with a rectangular (101) cross-section of 0.054×0.062 mm.

An Enraf-Nonius (CAD 4) computer-controlled four-circle diffractometer with equatorial geometry was used. The diffractometer was equipped with a graphite monochromator which gave Cu $K\alpha$ (1.5418 Å) radiation. The reflexions were scanned in the $\omega/2\theta$ mode. The scan interval, $\Delta\omega$, varied with the θ value of the reflexions according to $\Delta\omega = (1 + 0.15 \tan \theta)^\circ$.

The cell dimensions were determined from 30 reflexions whose θ values were measured with the diffractometer. The Laue symmetry and the systematic extinctions were inferred from preliminary Weissenberg photographs. Some crystal data are given in Table 1.

Table 1. *Crystal data*

$C_{11}H_8OS_2$, M.W. 220.3	
Orthorhombic, space group $Pn2_1a$ (No. 33)	
$a=15.1520$ (5) Å	$D_m=1.43$ g cm $^{-3}$
$b=4.6668$ (2)	$Z=4$
$c=14.2083$ (5)	$D_x=1.46$ g cm $^{-3}$
$V=1004.7$ Å 3	$\mu(\text{Cu } K\alpha)=43$ cm $^{-1}$

Intensities for $\frac{1}{8}$ of the reciprocal sphere were collected in a θ range of $3-75^\circ$ (1166 reflexions). Of these, 123 were considered unobserved, having $I < 2\sigma(I)$. Three standard reflexions were measured at intervals of 60 min. Their intensities showed a linear decay of 4% during the 100 h the crystal was exposed to the radiation. A numerical correction for this decrease was made.

The intensities were corrected for Lorentz, polarization and absorption effects: the transmission factors varied between 0.64 and 0.82. Systematic absences were: $hk0$ with $h=2n+1$ and $0kl$ with $k+l=2n+1$, indicating either the space group $Pn2_1a$ (No. 33) or $Pnma$ (No. 62); E statistics confirmed $Pn2_1a$. Symbolic addition was performed and an E map revealed the S atoms clearly.

Least-squares refinement of the positions of the S atoms followed by a difference synthesis revealed the positions of all non-hydrogen atoms. Another refinement of the positions of all these atoms followed by a difference synthesis indicated the positions of the H

* Part I: *Acta Chem. Scand.* (1974). B28, 681-688. Part II: *Acta Chem. Scand.* (1974). B28, 998-1002.

atoms. A final full-matrix least-squares refinement was performed with anisotropic temperature factors for the non-hydrogen atoms and isotropic for the hydrogens. The weight function was: $w_i^{-1} = \sigma^2 |F_o| + 0.0006 |F_o|^2 + 0.1$. The resulting agreement indices were: $R_1 = \sum |\Delta F| / \sum |F_o| = 0.0363$ and $R_2 = [\sum w_i (\Delta F)^2 / \sum w_i |F_o|^2]^{1/2} = 0.0446$. The goodness of fit, S , was 1.01. Scattering factors for the non-hydrogen atoms were from Doyle

& Turner (1968), those for the H atoms from Stewart, Davidson & Simpson (1965).

As the present space group lacks a centre of symmetry, serious errors in the positional parameters can result even for the light elements from the neglect of the imaginary component of the anomalous scattering (Cruickshank & McDonald, 1967). Therefore a correction for anomalous scattering was performed, with figures taken from Cromer & Liberman (1970). The agreement indices were now $R_1 = 0.0371$, $R_2 = 0.0453$ ($S = 1.03$), and for the inverse model $R_1 = 0.0453$, $R_2 = 0.0567$ ($S = 1.35$).

Although these results indicate that the corrections for anomalous scattering have not improved the fit, we have chosen to calculate distances and angles from the parameters obtained by the calculation giving $R_1 = 0.0371$. As a result of these corrections the bond distances in the molecule changed less than 2σ , though in such directions that the two halves of the molecule became more alike. The fractional coordinates of the atoms and their thermal parameters are given in Table 2.*

Discussion of the molecular structure

A stereo view of one molecule is given in Fig. 2. The distances, d , of the atoms to the best least-squares planes through the thiophene rings are listed in Table 3. For the marked atoms these distances are less than

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30835 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

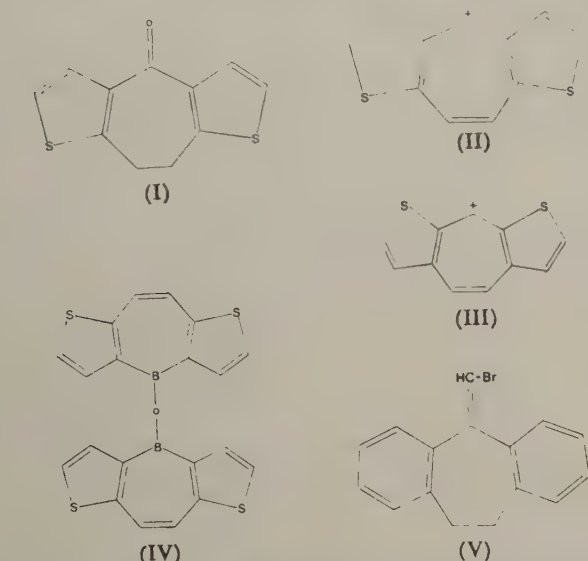


Fig. 1. Schematic drawings of the molecules: (I) 8,9-dihydro-4H-cyclohepta[1,2-b:5,4-b']dithiophene-4-one, (II) dithieno[1,2-b:5,4-b']tropylium tetrafluoroborate, (III) dithieno[2,1-b:5,4-b']tropylium perchlorate, (IV) bis-(4-dithieno[3,2:2',3'-f]borepinyl)ether, (V) 5-(bromoethylene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene.

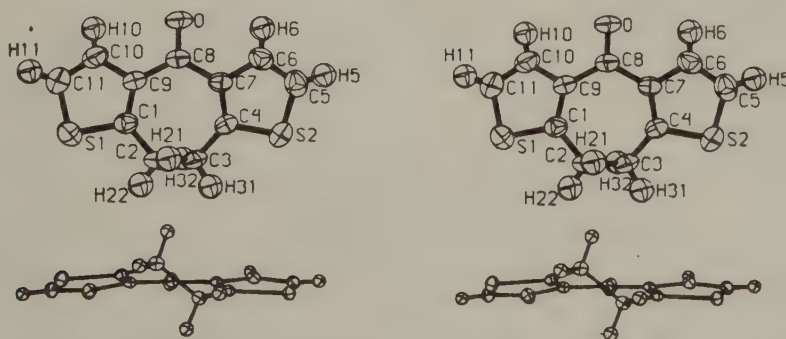


Fig. 2. A stereo view of one molecule of 8,9-dihydro-4H-cyclohepta[1,2-b:5,4-b']dithiophene-4-one viewed from two different directions. 50% probability ellipsoids are shown in the upper half of the figure.



Fig. 3. A stereo view of one molecule of 5-(bromomethylene)-10,11-dihydro-5H-dibenzo[a,d]cycloheptene.

Table 2. *Final positional and thermal parameters*

The estimated standard deviations are given in parentheses. The expression for the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. The β_{ij} values ($\times 10^4$) and the r.m.s. components ($\times 10^3$) are given separately below the other values.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> (Å) ²
S(1)	0.08939 (7)	−1	0.60689 (8)	
S(2)	0.46340 (7)	0.29765 (42)	0.72421 (7)	
C(1)	0.1823 (3)	−0.0425 (11)	0.6185 (3)	
C(2)	0.2146 (4)	0.0304 (13)	0.7155 (4)	
C(3)	0.3122 (4)	−0.0341 (12)	0.7260 (3)	
C(4)	0.3686 (3)	0.1675 (11)	0.6722 (3)	
C(5)	0.4901 (4)	0.5020 (13)	0.6289 (4)	
C(6)	0.4300 (4)	0.4743 (13)	0.5593 (4)	
C(7)	0.3602 (3)	0.2815 (11)	0.5832 (3)	
C(8)	0.2932 (3)	0.2084 (11)	0.5110 (3)	
C(9)	0.2152 (3)	0.0307 (10)	0.5322 (3)	
C(10)	0.1625 (4)	−0.0812 (13)	0.4572 (4)	
C(11)	0.0938 (4)	−0.2353 (16)	0.4858 (4)	
O	0.3050 (2)	0.2884 (14)	0.4306 (3)	
H(21)	0.202 (3)	0.225 (11)	0.726 (3)	3 (1)
H(22)	0.184 (4)	−0.079 (14)	0.755 (4)	6 (2)
H(31)	0.328 (3)	−0.020 (11)	0.793 (4)	5 (2)
H(32)	0.324 (3)	−0.223 (12)	0.709 (3)	4 (1)
H(5)	0.539 (4)	0.608 (13)	0.628 (4)	5 (2)
H(6)	0.432 (3)	0.573 (11)	0.500 (4)	4 (2)
H(10)	0.171 (3)	−0.046 (11)	0.395 (4)	4 (2)
H(11)	0.051 (4)	−0.328 (15)	0.449 (4)	6 (2)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
S(1)	49 (1)	676 (8)	66 (1)	−27 (3)	3 (1)	32 (3)
S(2)	51 (1)	624 (7)	56 (1)	3 (2)	−11 (1)	−31 (3)
C(1)	41 (2)	451 (22)	44 (3)	17 (6)	0 (2)	9 (6)
C(2)	59 (3)	561 (28)	35 (2)	4 (7)	11 (2)	26 (7)
C(3)	59 (3)	457 (23)	34 (3)	8 (7)	−7 (3)	17 (6)
C(4)	45 (2)	400 (18)	38 (2)	19 (6)	−2 (2)	−8 (6)
C(5)	48 (3)	593 (28)	71 (3)	−25 (7)	11 (3)	−48 (9)
C(6)	54 (2)	542 (25)	51 (3)	−14 (7)	12 (2)	−11 (7)
C(7)	47 (2)	391 (19)	38 (2)	12 (7)	6 (2)	0 (6)
C(8)	49 (2)	517 (24)	34 (2)	11 (6)	3 (2)	13 (6)
C(9)	46 (3)	430 (21)	34 (2)	18 (6)	−1 (2)	2 (5)
C(10)	59 (3)	650 (29)	42 (3)	1 (8)	−6 (2)	−10 (7)
C(11)	55 (3)	688 (31)	65 (3)	−21 (9)	−10 (3)	−16 (10)
O	67 (2)	1097 (28)	36 (2)	−58 (8)	−2 (2)	70 (7)

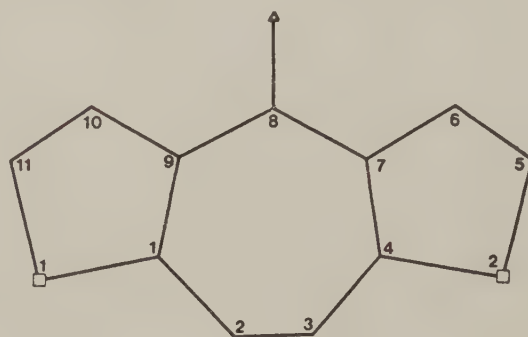
	<i>R</i> ₁	<i>R</i> ₂	<i>R</i> ₃
S(1)	221 (2) Å	256 (2) Å	290 (2) Å
S(2)	210 (2)	252 (2)	280 (2)
C(1)	204 (6)	213 (5)	236 (6)
C(2)	174 (6)	249 (7)	271 (6)
C(3)	177 (6)	229 (6)	266 (5)
C(4)	195 (6)	203 (6)	238 (6)
C(5)	222 (6)	229 (7)	303 (7)
C(6)	207 (5)	239 (6)	273 (6)
C(7)	190 (5)	206 (6)	240 (5)
C(8)	182 (5)	230 (6)	250 (6)
C(9)	187 (5)	209 (6)	241 (6)
C(10)	204 (5)	265 (6)	269 (7)
C(11)	225 (7)	277 (6)	282 (7)
O	174 (5)	267 (4)	367 (5)

3σ(*d*). C(2) and C(8) do not deviate very much from the best plane of the S(1) thiophene ring. For the S(2) thiophene ring, C(3) is situated close to the best plane, whereas the deviation of C(8) is quite large. The angle between the best planes of the thiophene rings is 158.2 (3)°. The torsional angle of C(2)–C(3) is 71 (1)°, and as seen from Fig. 2 the conformation around C(2)–C(3) is nearly staggered.

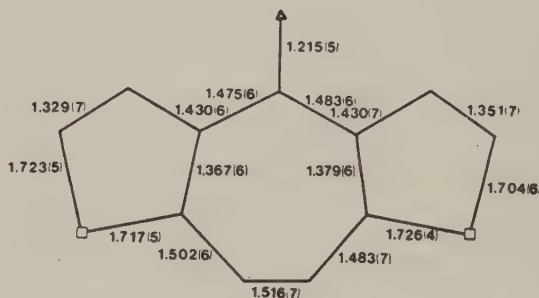
Table 3. *Least-squares planes*

Distances from the planes (Å) are $\times 10^3$. Atoms used to define the planes are marked with asterisks.

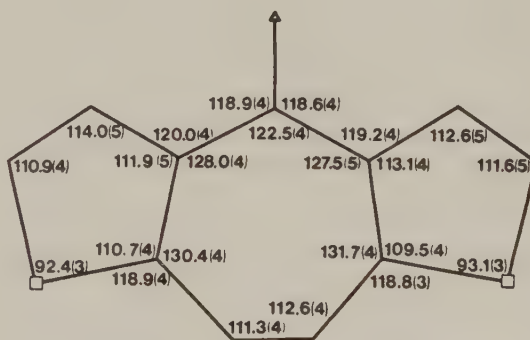
Plane I		Plane II	
S(1)	3*	S(2)	−2*
C(1)	−5*	C(5)	1*
C(9)	5*	C(6)	1*
C(10)	−3*	C(7)	−4*
C(11)	0*	C(4)	4*
C(2)	−23	C(3)	22
C(8)	−10	C(8)	−124
H(10)	−57	H(5)	−8
H(11)	−6	H(6)	21



□ S
▲ O



□ S
▲ O



□ S
▲ O

Fig. 4. Schematic pictures of one molecule of 8,9-dihydro-4H-cyclohepta[1,2-*b*:5,4-*b'*]dithiophene-4-one showing the non-hydrogen atoms. Numbering of the atoms, selected distances (Å) and angles (°) are presented. Remaining values can be found in Table 4. The estimated standard deviations are given in parentheses.

A benzene analogue of the present system, 5-(bromo-methylene)-10,11-dihydro-5*H*-dibenzo[*a,b*]cycloheptene, denoted (V) in Fig. 1, has been studied by X-ray methods (Larsson, 1970). A stereo view calculated from the data given by this author is presented in Fig. 3, from which it may be seen that the seven-membered ring has a deep boat form. The two C atoms adjacent to a benzene ring are situated in the best plane of the benzene ring. The planes of the benzenè rings form an angle of 119.9 (1)°. The torsional angle of C(2)–C(3) is 64 (4)° for the bromo compound. (The numbering of the atoms in the seven-membered ring is the same as that used for the thiophene compound.)

Table 4. Distances (Å) and angles (°) involving the hydrogen atoms

The estimated standard deviations are given in parentheses.

C(2)—H(21)	0.94 (5)	C(2)—C(3)—H(31)	109 (3)
C(2)—H(22)	0.89 (6)	C(2)—C(3)—H(32)	110 (3)
C(3)—H(31)	0.98 (5)	C(4)—C(3)—H(31)	108 (3)
C(3)—H(32)	0.93 (6)	C(4)—C(3)—H(32)	111 (3)
C(5)—H(5)	0.89 (6)	H(31)—C(3)—H(32)	106 (4)
C(6)—H(6)	0.96 (5)	S(2)—C(5)—H(5)	121 (4)
C(10)—H(10)	0.90 (5)	C(6)—C(5)—H(5)	127 (4)
C(11)—H(11)	0.94 (6)	C(5)—C(6)—H(6)	125 (3)
C(1)—C(2)—H(21)	107 (3)	C(7)—C(6)—H(6)	122 (3)
C(1)—C(2)—H(22)	106 (4)	C(9)—C(10)—H(10)	125 (4)
C(3)—C(2)—H(21)	112 (3)	C(11)—C(10)—H(10)	121 (4)
C(3)—C(2)—H(22)	110 (4)	S(1)—C(11)—H(11)	120 (4)
H(21)—C(2)—H(22)	110 (5)	C(10)—C(11)—H(11)	129 (4)

Bond lengths and angles are given in Table 4 and in Fig. 4. Corresponding distances and angles in the two halves of the molecule differ at most at a level of $\Delta/\sigma(\Delta)=3.0$. C(1)–C(2)–C(3) and C(2)–C(3)–C(4) are larger than the tetrahedral value. The S–C distances in the S(1) thiophene ring have $\Delta/\sigma(\Delta)=1$, while in the S(2) thiophene ring S(2)–C(4) is longer than S(2)–

C(5), $\Delta/\sigma(\Delta)=3$. Both for the S(1) and S(2) thiophene rings, the formal fused double bonds C(1)–C(9) and C(4)–C(7), respectively, are significantly longer than the purely thiophenic double bonds, C(10)–C(11) and C(5)–C(6). Differences of the same order of magnitude exist in the related unsaturated compounds dithieno-[2,1-*b*:5,4-*b'*]tropylium perchlorate, (III) in Fig. 1 (Aurivillius, 1974*a*), dithieno[1,2-*b*:5,4-*b'*]tropylium tetrafluoroborate, (II) (Andersson, J.-E., in preparation) and bis-(4-dithieno[3,2:2',3'-*f*]borepinyl)ether, (IV) (Aurivillius, 1974*b*). The bond distance of the conjugated carbonyl group is rather short, 1.216 Å. There are no intermolecular distances shorter than the sums of the pertinent van der Waals radii.

The author thanks Professor Bengt Aurivillius for many valuable discussions and Dr Christer Svensson for assistance with computer programs and diffractometer measurements. This work received financial support from the Swedish Natural Science Research Council.

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A

X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

V.* The Crystal Structure of 4*H*-Cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one

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$C_{11}H_6OS_2$ is monoclinic, space group $P2_1/c$, with $a = 9.3331$ (13), $b = 8.6930$ (18), $c = 11.9065$ (26) Å, $\beta = 110.098$ (14)° at 173 K, $Z = 4$. The structure was refined to an R of 0.041 for 1135 non-zero counter reflexions at 173 K. The molecule is almost planar; the planes of the two thiophene rings form an angle of 171.6 (8)°. Conjugation is indicated by the short formal C—C single bonds and the long C—O distance. The S—C bonds to the central ring are longer than the outer S—C bonds. A comparison of the detailed conformations of the present and similar molecules is made. The conformations are also correlated with their chemical properties.

Introduction

The cycloheptadithiophenes are tricyclic ring systems with aromatic properties. They have been synthesized and their aromatic properties studied by chemical and spectroscopic methods (Yom-Tov, 1972). A series with decreasing aromaticity is formed by three of these compounds: dithieno[1,2-*b*:5,4-*b'*]tropylium tetra-

* Part I: Aurivillius (1974*a*). Part II: Aurivillius (1974*b*). Part III: Andersson (1975). Part IV: Cynkier (1976).

fluoroborate (*E*) (Fig. 1), the title compound (*A*), and 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (*B*). The ion *E* has a relatively high stability to hydrolysis and was considered to be aromatic and planar. The C—O stretching frequency for the unsaturated ketone *A* is considerably lower than that for the saturated ketone *B* (Gronowitz, Yom-Tov & Michael, 1973). This suggests a high contribution of dipolar resonance form *F*, indicating aromatic character of the system. In view of the similarity in electronic structure between *E* and *F* this is in agreement with the high stability of the tropylium ion *E*. On the other hand, benzo-annulated tropylium ions are drastically less stable to hydrolysis, indicating a low degree of conjugation. In order to correlate chemical properties with molecular conformations the structures of the ketones *A* (this work) and *B* (Andersson, 1975) have been examined by X-ray diffraction and the tropylium ion *E* is under investigation.

X-ray diffraction work

A single crystal of *A* in the form of an approximately rectangular prism 0.07 × 0.07 × 0.20 mm was used for the experimental work. The X-ray data were collected on a four-circle diffractometer (Enraf-Nonius CAD-4) with equatorial geometry and graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å). The temperature of the crystal was kept at 173 K by a flow of cold nitrogen gas. Ice formation was prevented by heating the outer parts of the laminar nitrogen flow in the outlet nozzle and by keeping the whole diffractometer in a box filled with nitrogen (Danielsson, Grenthe & Oskarsson, 1976).

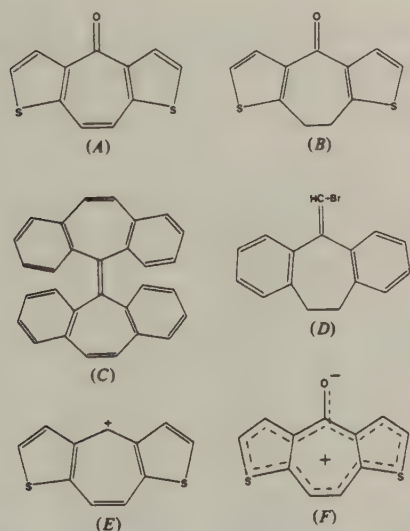


Fig. 1. Schematic drawings of the molecules: (*A*) 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*B*) 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*C*) 2,3;6,7;2',3';6',7'-tetrabenzozoheptafulvalene; (*D*) 5-(bromomethylene)-10,11-dihydro-5*H*-dibenzo[*a,b*]cycloheptene; (*E*) dithieno[1,2-*b*:5,4-*b'*]tropylium tetrafluoroborate; (*F*) resonance form.

$\text{C}_{11}\text{H}_6\text{O}\text{S}_{22}$ FW 218.30
Monoclinic, space group $P2_1/c$
 $a = 9.3331$ (13) Å
 $b = 8.6930$ (18)
 $c = 11.9065$ (26)
 $\beta = 110.098$ (14)°
 $V = 907.18$ Å³
 $Z = 4$

$$\begin{aligned} D_m &= 1.54 \text{ g cm}^{-3} \\ D_x &= 1.60 \\ \mu(\text{Mo } K\alpha) &= 5.3 \text{ cm}^{-1} \\ \lambda(\text{Mo } K\alpha_1) &= 0.70930 \text{ \AA} \\ T &= 173 \text{ K} \end{aligned}$$

	x	y	z	U
S(1)	0.80931 (11)	0.13326 (14)	0.48515 (10)	
S(2)	0.14049 (11)	0.37944 (14)	0.44851 (10)	
C(1)	0.6175 (5)	0.1685 (5)	0.4595 (4)	
C(2)	0.5827 (5)	0.2731 (5)	0.5381 (5)	
C(3)	0.4429 (5)	0.3231 (5)	0.5317 (4)	
C(4)	0.3011 (4)	0.2844 (5)	0.4416 (4)	
C(5)	0.0244 (5)	0.2893 (6)	0.3233 (4)	
C(6)	0.1023 (5)	0.1895 (5)	0.2785 (4)	
C(7)	0.2614 (5)	0.1837 (5)	0.3451 (4)	
C(8)	0.3601 (5)	0.0783 (5)	0.3084 (4)	
C(9)	0.5268 (5)	0.0819 (5)	0.3624 (4)	
C(10)	0.6169 (5)	-0.0119 (6)	0.3140 (4)	
C(11)	0.7678 (5)	0.0049 (6)	0.3682 (4)	
O	0.3004 (3)	-0.0148 (4)	0.2268 (3)	
H(2)	0.658 (5)	0.314 (5)	0.598 (4)	2.5 (10)
H(3)	0.431 (5)	0.394 (5)	0.587 (4)	3.1 (10)
H(5)	-0.084 (6)	0.319 (6)	0.297 (4)	3.5 (10)
H(6)	0.058 (4)	0.129 (5)	0.206 (4)	1.5 (7)
H(10)	0.573 (5)	-0.080 (5)	0.247 (4)	2.0 (9)
H(11)	0.856 (5)	-0.049 (5)	0.355 (3)	1.6 (8)

Fig. 2. The residual electron density in the vicinity of molecule *A* projected from a difference map. The maximum residual electron density is $0.31 \text{ e } \text{\AA}^{-3}$. Contours are drawn for 0.4, 0.5, ... times $0.31 \text{ e } \text{\AA}^{-3}$; *b* is pointing towards the reader. Fractional coordinates $\times 10^2$ along *b* for the highest peaks and for the atoms are given.

Discussion of the structure

A stereoview of the molecule is shown in Fig. 3 and the packing of the molecules is shown in Fig. 4. The molecules are arranged in pairs, within which they are related by a center of symmetry. The distance between the best planes (IV in Table 3) of the molecules in such a pair is 3.54 Å. The shortest intermolecular distances are given in Table 4. Only O—H is somewhat shorter than the van der Waals distance.

The deviations of atoms from some least-squares planes, and interplanar angles are given in Table 3. The deviations of the atoms of the thiophene rings from their respective planes are small, but significant. The atoms in the cycloheptatrienone ring, C(2), C(3) and C(8), nearest the respective thiophene rings show considerably larger deviations from these planes. The

torsion angles are given in Fig. 5(a). Starting with the pair S(1)[C(1)C(9)]C(10) and S(2)[C(4)C(7)]C(6) of the thiophene rings and going clockwise for comparison, a striking similarity between the torsion angles is revealed. This agreement and the deviations of C(2), C(3) and C(8) might be seen as the result of a minor twist of the whole molecule lengthwise.

The seven-membered ring has a boat conformation, as can be seen from the deviations from plane III (Table 3). The conformation is distorted in the way mentioned above, and for this reason a comparison of the torsion angles of the right and the left sides of ring III does not give good agreement (Fig. 5a). Some other planes (IV–VII) in the central ring support this presumption (Table 3). The angle between planes I and II is $171.6(8)^\circ$.

Bond lengths and angles are given in Fig. 5(a). The

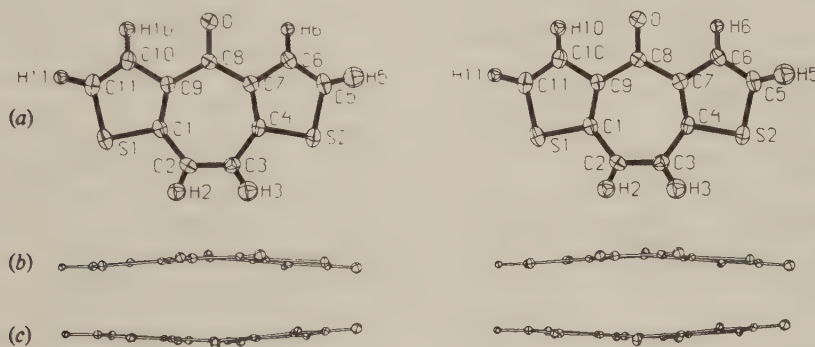


Fig. 3. A stereoview of molecule *A* from three different directions. In (a) 50% probability ellipsoids are shown, in (b) C(2) and C(3) point towards the reader and in (c) O points towards the reader.

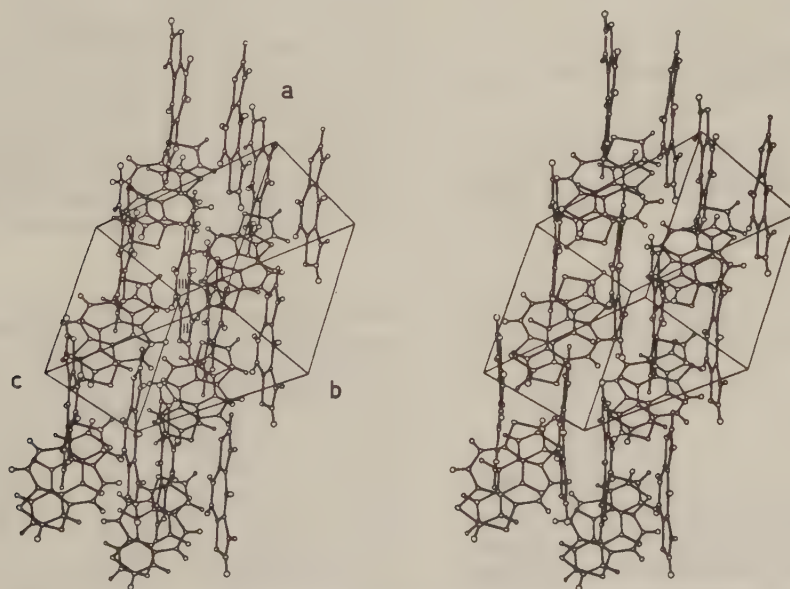


Fig. 4. A stereoview of the stacking of molecules *A*. The rings of the molecule in the asymmetric part of the unit cell are marked according to Fig. 5(a).

Table 3. *Least-squares planes in A*

Deviations ($\times 10^3$ Å) of the atoms from the planes, and the angles between them are given. Atoms used to define the planes are marked with asterisks. Weights proportional to the atomic numbers were used.

Plane I		Plane II		Plane III	
S(1)*	1	S(2)*	4	C(1)*	-43
C(1)*	2	C(4)*	-12	C(2)*	14
C(9)*	-7	C(7)*	7	C(3)*	41
C(10)*	10	C(6)*	4	C(4)*	-27
C(11)*	-8	C(5)*	-10	C(7)*	-40
C(2)	31	C(3)	-45	C(8)*	61
C(8)	-37	C(8)	40	C(9)*	-6
H(10)	15	H(6)	-32	O	174
H(11)	36	H(5)	-13	H(2)	20
				H(3)	65

Plane IV		Plane V	
S(1)*	-76	C(9)*	35
S(2)*	-27	C(10)*	-30
C(1)*	35	C(11)*	-117
C(2)*	126	O*	165
C(3)*	155	H(2)	153
C(4)*	57	H(3)	202
C(5)*	-172	H(5)	-255
C(6)*	-128	H(6)	-225
C(7)*	7	H(10)	-32
C(8)*	85	H(11)	-137

Plane VI	Plane VII	Angles (°) between the planes	
C(1)*	4	C(1)*	-12
C(2)*	-8	C(2)	58
C(3)*	8	C(3)	88
C(4)*	-4	C(4)*	12
H(2)	-44	C(7)*	-14
H(3)	-16	C(8)	77
		C(9)*	14
		O	180
		H(2)	71
		H(3)	121

I-II	171.6 (8)†
I-III	176.1 (17)
II-III	175.4 (17)
VII-V	174.7 (32)
VII-VI	176.3 (40)
V-VI	170.9 (39)

† The e.s.d.'s are calculated without considering covariances, in contrast to Waser, Marsh & Cordes (1973).

Table 4. *Shortest intermolecular distances (Å) between atoms in A*

S-S	3.871 (2)	O-C	3.349 (5)
S-O	3.345 (3)	O-H	2.42 (5)
S-C	3.508 (4)	C-C	3.422 (6)
S-H	3.03 (4)	C-H	2.85 (4)
O-O	>4.0	H-H	2.50 (6)

distances and angles for corresponding bonds in the right and left parts of the molecule are not significantly different. The half-normal probability plot method (Hamilton, 1974) indicates that the standard deviations of the bonds and angles are overestimated by a factor of 0.7.

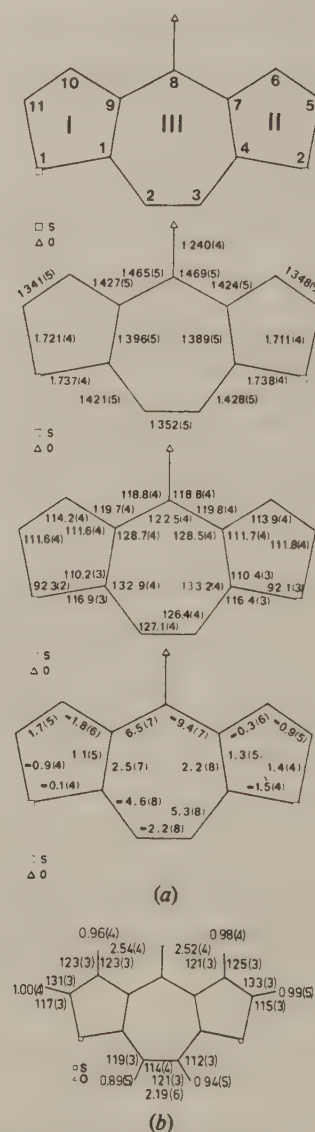


Fig. 5. Compound A. (a) Schematic diagrams showing the non-hydrogen atoms. The numbering of the ring system and the atoms, as well as selected distances (Å), bond angles (°) and torsion angles (°) are presented. The e.s.d.'s are given in parentheses. (b) Distances (Å) and angles (°) to H atoms.

Thus, we conclude that the molecule has an approximate mirror plane. Within each half of the molecule the S-C bond to the central ring is longer than the outer S-C bond. The formal double bonds of the central ring C(1)-C(9) and C(4)-C(7) are longer than the other double bonds of the molecule, all of which have the same length. Similarly, the formal single bonds of the central ring C(7)-C(8) and C(8)-C(9) are longer than the other single bonds. The C-O distance is rather long, 1.240 (4) Å. The angles of the ring systems differ from the ideal values for five- and seven-membered rings, especially in ring III at C(1), C(4) and C(8).

The H atoms are not significantly out of their respective planes (Table 3). Bond distances and angles involving H atoms are given in Fig. 5(b).

Comparison with *B*

In the light of the present structure (*A*), the corresponding cycloheptadienone structure, 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (*B* in Fig. 1) (Andersson, 1975), will be discussed. For convenience a stereoview of *B* is reproduced in Fig. 6. From this drawing and Fig. 3 it can be seen that the conformations of the compounds are remarkably similar; *B* might be thought of as resulting from *A* by exchanging the double bond C(2)—C(3) for a single bond, thereby twisting the rigid thiophene parts to each side. *A* has a slightly bent shape, but it is difficult to decide whether this deviation from the plane is transferred to *B*.

The precision in the determination of the structure of *A* is much higher than that of *B* (see below). In *B* the thiophene rings are planar within experimental error. In fact, the deviations from the planes I and II are markedly less in *B* than in *A*. However, C(8) (ring III) in *B* has a quite large deviation of 0.12 Å from plane I. Thus *B* is distorted from idealized C_2 symmetry, possibly depending on thermal motion. The cycloheptadienone ring in *B* has a twisted form with an angle between the thiophene planes of 158.2(3)°. The torsion angles of *B* (Fig. 7) have about the same values as those of *A*, except for the C(1)—C(2)—C(3)—C(4) bonds.

The bond distances in *B* show differences between the right and left parts of the molecule; a half-normal probability plot indicated that the standard deviations of the bonds are underestimated by a factor of 1.6. This is taken into consideration in the comparison of *A* and *B*. The C(1)—C(2)—C(3)—C(4) bonds in *B* compared to those in *A* are quite different, but some other smaller differences also exist. Thus, in *B* the formal double bond C(1)—C(9) in the seven-membered ring, the carbonyl group and the annelated S(1)—C(1) bonds are

shorter than those in *A*. Some caution is appropriate as the structure of *A* in contrast to *B* was determined at low temperature and is likely to have smaller thermal motion. Large thermal motion of the molecules can give systematic errors often appearing as an apparent shrinkage of bond lengths. The angles in *A* and *B* show only small differences; the values of C(2)—C(1)—C(9) and C(3)—C(4)—C(7) in *B* are significantly smaller, however.

Conformations and properties

For comparison of the seven-membered ring in different conformations (planar and boat forms), two more compounds (*C* and *D* in Fig. 1) will be discussed. *syn*-TBHF (*C*) (Dichmann, Nyburg, Pickard & Potworowski, 1974) has three double bonds in the central ring, which is also the case for *A*. 5-(Bromomethylene)-10,11-dihydro-5*H*-dibenzo[*a,b*]cycloheptene (*D*) (Larsson, 1970; stereoview, Andersson, 1975) has two double bonds (as in *B*). The seven-membered ring in the boat form (*C*) has almost planar ethylene units and torsion mainly in the single bonds. *A* is only slightly twisted in the single bonds. The same is valid for *D* compared to *B* if the bonds C(1)—C(2)—C(3)—C(4) are not taken into account. This indicates a greater overlap of *p* orbitals in *A* and *B* compared to *C* and *D*, and this is especially marked for C(7)—C(8) and C(8)—C(9),

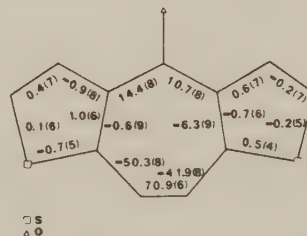


Fig. 7. Compound *B*. A schematic diagram showing the torsion angles (°). The numbering of the ring system and the atoms are as in Fig. 5(a).

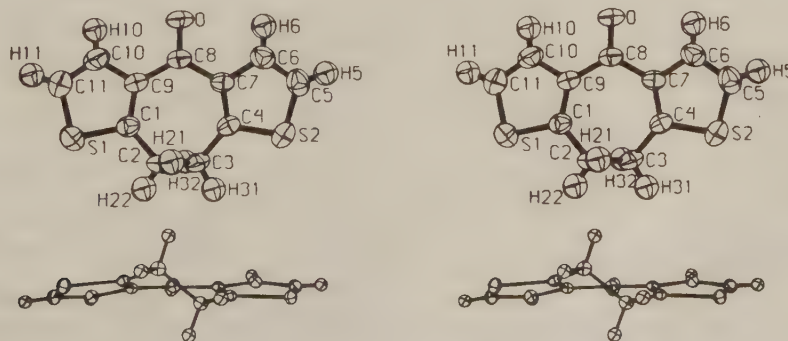


Fig. 6. Compound *B*. A stereoview of one molecule viewed from two directions. 50% probability ellipsoids are shown in the upper drawing.

where, in fact, the bond distances do not differ very much between the planar and boat forms.

The bond lengths of *A*, *B* and *C* are compared with those accepted for single and double bonds in Table 5. For *A*, the lengths of the double bond C(1)–C(9) and the single bond C(1)–C(2) are equal to the lengths of an aromatic bond and of C–C in graphite respectively. The double bond C(2)–C(3) is longer, and the single bond C(7)–C(8) shorter than the corresponding reference values. This indicates that there is some conjugation in the system. The short single bond C(1)–C(2) is remarkable. For *B* the bond lengths are closer to the reference values. The C–O and the C(1)–C(9) distances are shorter compared to those of *A*, in good agreement with the C–O stretching frequencies. This is an indication of less delocalization for *B* than for *A*. Also, for *C* the bond distances are clearly closer to the reference values than for *A* [except for C(1)–C(9)] and this is particularly apparent for C(1)–C(2). The torsion angles are much greater for *C*. Thus the bond alternation and torsion of the bonds indicate decreasing conjugation in the order *A/B* and *A/C*. For all the compounds the distances C(1)–C(9) and C(8)–C(9) in

the central ring are longer than the other double and single bonds respectively. The annelated S–C bonds of *A* are longer than the outer S–C bonds.

In the approximately planar molecules *A* and *B*, the angle at the carbonyl bond C(7)–C(8)–C(9) is 122.5° and the mean value of the other angles of the seven-membered ring is 129.5°. In the central ring of *C* (boat form), the C(7)–C(8)–C(9) angle is 114.3° and the mean value of the other angles (123.6°) is much less than in *A* and *B*. Thus, angular strain is much less in the boat form. The annelation of a five-membered ring such as thiophene decreases the angular strain, as pointed out by Gronowitz *et al.* (1973). This is more pronounced than for a six-membered ring, such as benzene. The angle C(2)–C(1)–C(9) of *A* (132.9°) is greater than the corresponding angle of *B* (130.4°).

Intramolecular interactions are not large in *A*, *B* and *C*. They are mainly between the *peri* atoms of the central ring and the annelated rings and are thus dependent on their types. However, steric factors such as intramolecular H–H and H–C interactions are probably important in determining the conformations of *C* and *D*. In a fictitious planar form of *C* there would be large interactions, assuming normal C–H distances and C–C–H angles. In a boat form these interactions, as well as the angular strain, are minimized and this is probably also valid for *D*. Such interactions are small in the thiophene compounds.

Thus the properties of the above compounds, observed by chemical and spectroscopic methods, agree well with the detailed geometry of the molecules in the crystalline state. Preliminary structural results on the tropylium ion *E* (Fig. 1) also follow these trends in properties and structural details.

The author thanks Professor Bengt Aurivillius for valuable discussions, Dr Karin Aurivillius for reading the manuscript and Dr Åke Oskarsson for assistance with the low-temperature apparatus. This work received financial support from the Swedish Natural Science Research Council.

Table 5. Mean values of bond distances (Å)

The e.s.d.'s for *A* and *B* are multiplied by 0.7 and 1.6 respectively (see text). Notation: *s* = single bond, *d* = double bond. The reference distances are taken from *International Tables for X-ray Crystallography* (1962) and from Kitaigorodsky (1973).

Seven-membered ring

Compound	<i>d</i> or <i>s</i>	C(2)–C(3)	C(1)–C(9) C(4)–C(7)	C(1)–C(2) C(3)–C(4)	C(7)–C(8) C(8)–C(9)
			<i>d</i>	<i>s</i>	<i>s</i>
<i>A</i> (173 K)	1.352 (4)		1.393 (3)	1.425 (3)	1.467 (3)
<i>B</i> (295 K)	1.516 (12)		1.373 (7)	1.493 (8)	1.479 (7)
<i>C</i> (<i>c.a.</i> , 295 K, molecule 1)	1.341 (5)		1.406 (4)	1.456 (4)	1.489 (3)
Reference bonds	Double (simple) 1.337 (6) Single (partial) 1.507		Aromatic 1.395 (3)	Graphite 1.4210 (1)	Single (partial) 1.476

Thiophene rings and the carbonyl bond

		C(10)–C(11) C(5)–C(6)	C(9)–C(10) C(6)–C(7)
		<i>d</i>	<i>s</i>
<i>A</i> (173 K)		1.345 (4)	1.426 (4)
<i>B</i> (295 K)		1.340 (8)	1.430 (8)
		S(1)–C(1) S(2)–C(4)	S(1)–C(11) S(2)–C(5)
		<i>s</i>	<i>s</i>
<i>A</i> (173 K)		1.738 (3)	1.716 (3)
<i>B</i> (295 K)		1.722 (6)	1.714 (7)
			C–O
			1.240 (3) 1.215 (8)

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E

X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

X. The Crystal Structure of Dithieno[1,2-*b*:5,4-*b'*]tropylium Tetrafluoroborate at 143 and 295 K

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Abstract

(C₁₁H₇S₂)⁺BF₄[−] is triclinic, space group *P*1̄, with *a* = 7.1949 (12), *b* = 8.7203 (12), *c* = 9.5967 (20) Å, *α* = 105.787 (15), *β* = 99.074 (13), *γ* = 96.817 (13)° at 143 K, *Z* = 2. The structure was refined to an *R* of 0.043 for 1448 non-zero counter reflexions at 143 K. The cation is almost planar: the angle between the planes of the two thiophene rings is 175.3 (4)°. Aromatic character is indicated by the relatively uniform C–C lengths. The S–C bonds are equal. The BF₄[−] ion is disordered and has been described by two different orientations.

Introduction

The title compound is composed of dithienotropylium cations and BF₄[−] anions. The cation has aromatic character and is relatively stable to hydrolysis. The chemical properties of tropylium ions substituted with thiophene rings have been studied by Yom-Tov (1972). The structure of one of these compounds of aromatic character, dithieno[2,1-*b*:4,5-*b'*]tropylium perchlorate, has been determined (Aurivillius, 1974) and the cation found to be planar.

The present compound (*E*.BF₄[−], Fig. 1) is the first of a series (*E*,*A*,*B*), the structures of which have been determined. The second (*A*) is 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (Andersson, 1978) and the third (*B*) is 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one (Andersson, 1975). Chemical and

spectroscopic data indicate a decrease of aromaticity from the first to the last compound, and the structures of *A* and *B* have been correlated with their chemical properties (Andersson, 1978). With the present structure determination the series will be completed.

The packing of the ions has been studied. The BF₄[−] ions are disordered, which is also the case for ClO₄[−] in the compound studied by Aurivillius (1974). The present structure was determined at both 143 and 295 K.

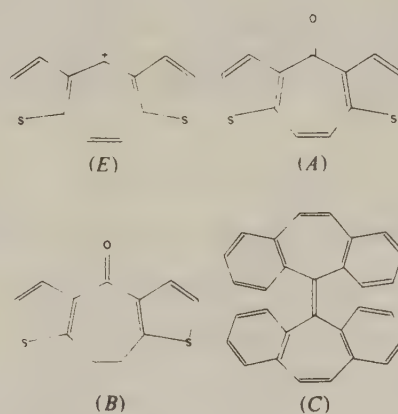


Fig. 1. Schematic drawings of the molecules: (*E*) dithieno[2,1-*b*:5,4-*b'*]tropylium tetrafluoroborate; (*A*) 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*B*) 8,9-dihydro-4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-one; (*C*) 2,3:6,7:2':6':7'-tetra-benzoheptafulvalene.

X-ray diffraction work

Only the experimental details at 143 K are given here. The experiment at 295 K was similar.*

A single crystal of $E\text{-BF}_4^-$ of regular form, and with a volume of $4.7 \times 10^{-3} \text{ mm}^3$, was used. Cell dimensions and intensities were determined on a four-circle diffractometer (Enraf-Nonius CAD-4) with equatorial geometry and Zr-filtered Mo K radiation ($\lambda = 0.71073 \text{ \AA}$). A flow of cold nitrogen gas was used to keep the crystal at 143 K (Danielsson, Grenthe & Oskarsson, 1976). Some crystal data are given in Table 1. The intensities of 2362 reflexions of which 910 had $I < 2\sigma_c(I)$ were measured (Lehmann & Larsen, 1974).*

Determination and refinement of the structure

The structure was solved from Weissenberg data by symbolic addition. The refinement was continued with diffractometer data* obtained at 295 K. A second crystal* and graphite-monochromatized Cu K radiation ($\lambda = 1.5418 \text{ \AA}$) were used. The final refinement was similar to the one at 143 K (*cf.* below). The temperature factors of the H atoms could not be refined and were given the value of $4.5 \text{ \AA}^2$.* The resulting $R = 0.084$ and $R_w = 0.111$, $S = 1.45$.

The results of the room-temperature determination were used as a starting point for refinement with the low-temperature data.* The intensities were corrected

for Lorentz and polarization effects but not for absorption.

In the final full-matrix least-squares refinement of the 143 K data, the function minimized was $\sum w(\Delta|F|)^2$, where $\Delta|F| = |F_o| - |F_c|$. The weight function was $w^{-1} = \sigma_c^2(|F_o|) + 0.0016|F_o|^2 + 0.30$. Scattering factors were those of Doyle & Turner (1968) for non-hydrogen atoms, and for H those of Stewart, Davidson & Simpson (1965). The anomalous-scattering factors of Cromer & Liberman (1970) were used for non-hydrogen atoms. The BF_4^- ion was inserted in two different orientations, the occupancy factors (sum = 1) of which were refined relative to each other. Anisotropic temperature factors were refined,* except for F and H atoms, which were treated isotropically.

The final $R = \sum |\Delta|F| / \sum |F_o| = 0.043$ and $R_w = [\sum w(\Delta|F|)^2 / \sum w|F_o|^2]^{1/2} = 0.057$. The goodness of fit, $S = [\sum w(\Delta|F|)^2 / (m - n)]^{1/2} = 1.01$, where m is the number of observations and n the number of parameters. The final coordinates are given in Table 2.* A comparison of observed and calculated structure factors showed no apparent extinction. The residual electron density was <0.67 and $0.28 \text{ e \AA}^{-3}$ in the region of the BF_4^- and the tropylium ion respectively. The thermal parameters of the S and C atoms were explained as resulting from the motion of a rigid molecule (Schomaker & Trueblood, 1968). (No details of the calculations are given here.)

* See deposition footnote.

* Additional experimental and refinement details at 143 and 295 K, tables of positional parameters, least-squares planes and distances and angles involving H atoms and angles in the dithienotropylium ion at 295 K, lists of structure factors, thermal parameters, details of the crystal habit and distances and angles in the BF_4^- ion at 295 and 143 K and details of additional least-squares planes at 143 K, have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34178 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Crystal data

$(\text{C}_{11}\text{H}_7\text{S}_2)^+ \text{BF}_4^-$, FW 290.1, triclinic, space group $P\bar{1}$

	143 K	295 K
a	7.1949 (12) Å	7.3124 (6) Å
b	8.7203 (12)	8.6753 (5)
c	9.5967 (20)	9.6675 (5)
α	105.787 (15)°	105.589 (4)°
β	99.074 (13)	98.794 (6)
γ	96.817 (13)	96.893 (7)
V	563.82 Å ³	575.36 Å ³
$Z = 2$	$\mu(\text{Mo K}\alpha) = 0.48 \text{ mm}^{-1}$ (143 K)	
$D_m = 1.66 \text{ Mg m}^{-3}$	$\lambda(\text{Mo K}\alpha) = 0.70930 \text{ \AA}$ (143 K)	
$D_x = 1.67$	$\mu(\text{Cu K}\alpha) = 4.4 \text{ mm}^{-1}$ (295 K)	
	$\lambda(\text{Cu K}\alpha) = 1.54051 \text{ \AA}$ (295 K)	

Table 2. Positional and isotropic thermal parameters with e.s.d.'s in parentheses (143 K)

The expression for the isotropic temperature factor is $\exp[-8\pi^2 U (\sin \theta/\lambda)^2]$.

Occupancy $\%$	x	y	z	$8\pi^2 U (\text{\AA}^2)$
S(1)	0.25351 (15)	0.42078 (12)	0.49981 (11)	
S(2)	0.14294 (16)	0.85026 (12)	0.04346 (13)	
C(1)	0.2438 (5)	0.5132 (5)	0.3608 (5)	
C(2)	0.1955 (6)	0.6696 (5)	0.3897 (5)	
C(3)	0.1725 (6)	0.7607 (5)	0.2933 (5)	
C(4)	0.1885 (5)	0.7178 (5)	0.1442 (5)	
C(5)	0.1900 (7)	0.7229 (6)	-0.1136 (5)	
C(6)	0.2393 (6)	0.5855 (5)	-0.0951 (5)	
C(7)	0.2412 (6)	0.5750 (5)	0.0532 (4)	
C(8)	0.2893 (6)	0.4417 (5)	0.0959 (4)	
C(9)	0.2918 (5)	0.4115 (5)	0.2323 (5)	
C(10)	0.3419 (6)	0.2629 (5)	0.2573 (5)	
C(11)	0.3254 (6)	0.2535 (5)	0.3930 (5)	
F(12)	64 (4)	0.4112 (9)	0.0141 (8)	0.6349 (11)
F(13)	64 (4)	0.1160 (8)	-0.0292 (7)	0.6985 (12)
F(14)	64 (4)	0.2538 (14)	0.2206 (7)	0.7128 (7)
F(15)	64 (4)	0.3787 (15)	0.0924 (7)	0.8772 (6)
F(17)	36 (4)	0.4319 (16)	-0.0037 (13)	0.6740 (19)
F(18)	36 (4)	0.3214 (30)	0.0900 (13)	0.8823 (12)
F(19)	36 (4)	0.1188 (13)	-0.0352 (11)	0.6599 (19)
F(20)	36 (4)	0.3047 (27)	0.2292 (13)	0.7181 (12)
B		0.2926 (7)	0.0731 (6)	0.7302 (5)
H(2)		0.186 (8)	0.718 (7)	0.486 (7)
H(3)		0.137 (6)	0.859 (5)	0.324 (5)
H(5)		0.170 (8)	0.746 (7)	-0.202 (7)
H(6)		0.268 (8)	0.504 (7)	-0.166 (6)
H(8)		0.325 (7)	0.352 (6)	0.017 (6)
H(10)		0.376 (7)	0.199 (6)	0.195 (6)
H(11)		0.350 (9)	0.175 (8)	0.436 (7)
				4.7 (15)

A refinement in which anisotropic temperature factors were used only for the S atoms, but in other details similar to the final one, gave $R = 0.048$ and $R_w = 0.063$, $S = 1.09$. The residual electron density was $<0.66 \text{ e } \text{\AA}^{-3}$.

Discussion of the structure at 143 K

The compound is ionic, and composed of dithienotropylium cations (Fig. 2) and BF_4^- anions. The cation has no inherent crystallographic symmetry. The structure consists of planes of tilted tropylium ions at right angles to a with BF_4^- ions in the space between four tropylium ions (Fig. 3a). Parallel to the ac plane, layers of tropylium ions with layers of BF_4^- ions in between can be distinguished.

From crystallographic symmetry the best planes of the tropylium ions are all parallel (Fig. 3b), and within a layer the distance between the planes is $3.347 \text{ \AA}$. The planes of a neighbouring layer are 1.169 and $2.179 \text{ \AA}$ from a tropylium ion plane. The shortest contacts between the tropylium ions are given in Table 3. Most of these contacts are within a layer.

The BF_4^- ion is disordered, with two predominant orientations. The shortest distances between BF_4^- ions (Table 3) are found in the approximate ac plane. Between the layers in the direction of these planes the distances are considerably greater.

The distances from the BF_4^- ions to the tropylium ions (Table 3) are short relative to the van der Waals distances and the distances between ions of the same charge.

Table 3. Intermolecular distances ($\text{\AA}$) at 143 and 295 K

Van der Waals radii (Bondi, 1964) and upper limits at 143 and 295 K are given. This is followed by the atoms, the distance between them at 143 K and the increase in distance ($\times 10^3$) from 143 to 295 K. Distances between layers are marked with an asterisk.

Distances between cations				Distances between anions			
VdW 3.5	<4.00	<4.00		VdW 3.0	<3.90	<3.83	
S(1)—S(1)	3.650 (2)	31		F(12)—F(12)	3.027 (18)	110	
S(2)—S(2)*	3.697 (2)	72		F(15)—F(15)	3.554 (13)	91	
VdW 3.45	<3.69	<3.71		F(19)—F(19)	3.513 (29)	>487	
S(1)—C(1)	3.573 (4)	89		F(17)—F(17)	3.640 (31)	>360	
S(2)—C(8)	3.591 (4)	18		F(12)—F(17)	3.317 (18)	342	
S(2)—C(10)*	3.611 (4)	17		F(13)—F(19)	3.801 (18)	—398	
S(1)—C(2)	3.621 (4)	71		F(15)—F(18)	3.709 (16)	>291	
VdW 2.95	<3.34	<3.44		Distances between different ions			
S(1)—H(6)	3.07 (6)	570		VdW 3.25	<3.35	<3.41	
S(2)—H(10)*	3.13 (5)	180		F(14)—S(1)	3.028 (6)	45	
S(1)—H(2)	3.29 (5)	—30		F(20)—S(1)	3.020 (10)	153	
VdW 3.4	<3.59	<3.65		F(18)—S(2)	3.187 (12)	—70	
C(5)—C(9)	3.428 (5)	69		F(18)—S(2)	3.592 (20)	—338	
C(6)—C(8)	3.429 (5)	80		VdW 3.2	<3.20	<3.23	
C(7)—C(7)	3.447 (7)	44		F(12)—C(11)	3.159 (7)	13	
VdW 2.9	<3.31	<3.31		F(14)—C(3)	3.082 (10)	93	
C(6)—H(8)	3.05 (5)	160		F(17)—C(11)	2.950 (11)	—11	
C(8)—H(6)	3.10 (6)	210		F(17)—C(10)	3.089 (12)	—158	
VdW 2.4	<3.00	<3.11		VdW 2.7	<2.41	<2.47	
H(3)—H(11)*	2.82 (8)	48		F(18)—H(8)	2.30 (5)	110	
H(2)—H(5)	2.96 (8)	100					

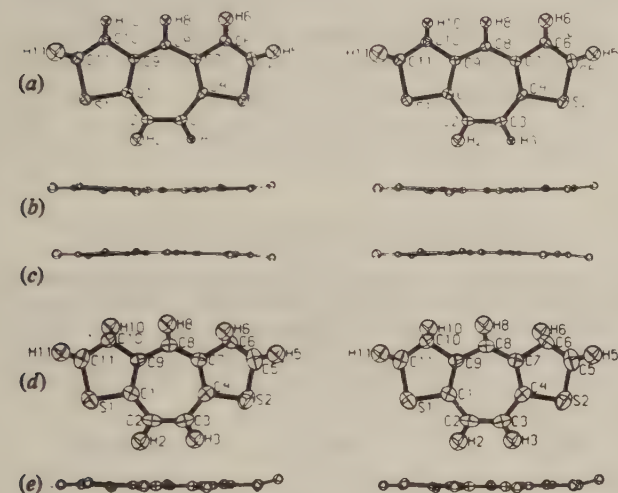


Fig. 2. A view of the cation E from three different directions and at two different temperatures; (a), (b), (c) at 143 K and (d), (e) at 295 K. In (a) and (d) 50% probability ellipsoids are shown, in (b) and (e) C(2) and C(3) point towards the reader and in (c) C(8) points towards the reader.

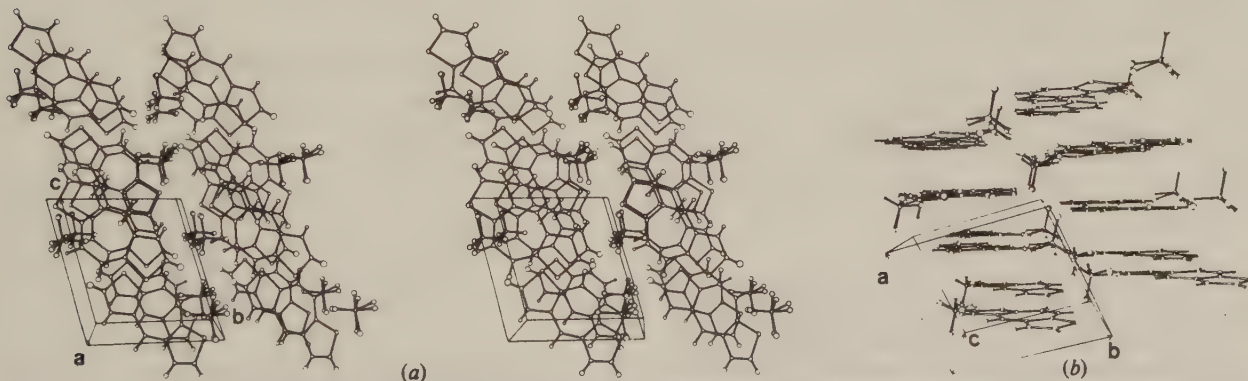


Fig. 3. (a) A stereoview of the stacking of ions E at 143 K with a pointing towards the reader. (b) A view of the stacking of ions E at 143 K with the planes of cations seen from the side.

Fig. 5. The dithienotropylium ion *E* at 295 K. Distances (Å) are presented. The numbering of the ring system and the atoms is as in Fig. 4.

Conformation

The deviations of the atoms from the thiophene rings are significant for plane I but not for plane II. The atoms C(2) and C(8) in the cycloheptatrienylium ring deviate greatly from plane I, in contrast to the deviations of C(3) and C(8) from plane II. There is a minor twist of ring I. The seven-membered ring has a boat conformation distorted by a twist. The angle between planes I and II is $175.3(4)^\circ$.

The statistical distribution of chemically equivalent bond distances and angles (Fig. 4a) in the cation indicates that the e.s.d.'s are overestimated by a factor of 0.7 and that systematic deviations occur (Hamilton, 1974). All distances on the left side except one are longer than the corresponding ones on the right and the same features are found at 295 K. The e.s.d.'s multiplied by a factor of 1.7 have been used when calculating mean values for Table 5.

Within each half of the cation the S—C bonds are not significantly different. The bond lengths of the central ring lie within a smaller interval than those of the thiophene rings. The formal single bonds C(1)—C(2), C(3)—C(4) and C(7)—C(8), C(8)—C(9) of the central ring are of about the same length. The angles differ only

slightly from the ideal values for five- and seven-membered rings. The H atoms* (Figs. 2, 4b) are not significantly out of their respective planes (Table 4).

The e.s.d.'s for the BF_4^- ion are underestimated by a factor of 2.2 and the mean B—F distance is $1.397(8) \text{ \AA}$.

Comparison with A

The structure of *A* (Fig. 1) was also determined at low temperature (173 K), and the precision is high with no apparent systematic deviations. A stereoview of *A* is given in Andersson (1978). The conformations of *E* and *A* are very much alike. *A* is slightly more bent than *E* and has an approximate mirror symmetry with a twist and both thiophene rings non-planar, in contrast to *E* for which ring II is planar. In both structures the seven-membered ring has a twisted-boat form. The angles between planes I and II are $175.3(4)^\circ$ for *E* and $171.6(8)^\circ$ for *A*.

Conformations and properties

E is the first in the series *E*, *A*, *B* of decreasing aromatic properties (Andersson, 1978). *E* and *A* are nearly planar and *B* has a twisted form.

The bond lengths are compared to those accepted for single and double bonds in Table 5. Another molecule (*C*), 2,3:6,7:2',3':6',7'-tetrabenzoheptafulvalene (Dichmann, Nyburg, Pickard & Potworowski, 1974), included in Table 5 and Fig. 1 for comparison, has the seven-membered rings in the boat form. The bond lengths of the central ring of *E* are closer to those of aromatic compounds and of graphite than those of the other compounds of the series, indicating a higher degree of conjugation. C(1)—C(9) and C(4)—C(7) are longer than the formal single bonds C(1)—C(2), C(3)—C(4) and C(7)—C(8), C(8)—C(9). The spread of the bond distances increases in a regular way through the series *E*, *A*, *B*. The C—C distances in the thiophene rings, in contrast, become more alike, and the S—C distances more different in the series. *C* is to be primarily compared to *A* as they have similar electronic structures.

The C(7)—C(8)—C(9) angle in *E* is much greater than in *A*, $129.1(4)^\circ$, and the mean of the other angles in the central ring is 128.5° , indicating slightly less angular strain than in *A*, but much higher than that in *C*. The angles at the thiophene rings are smaller for *E* than for *A*. In the thiophene rings the angles at C(5), C(6) and C(10), C(11) are more alike in *E* than in *A*.

Intramolecular interactions are not large in *E*, and are mainly H—H and H—C interactions (Fig. 4b). In *C*

Table 5. Mean values of bond distances ($\text{\AA}$)

The e.s.d.'s for *E*, *A* and *B* are multiplied by 1.7, 0.7 and 1.6, respectively (see text). Notation: *s* = single bond, *d* = double bond. The reference distances are taken from *International Tables for X-ray Crystallography* (1962) and from Kitaigorodsky (1973).

Seven-membered ring

Compound	C(2)—C(3) <i>d</i> or <i>s</i>	C(1)—C(9) C(4)—C(7) <i>d</i>	C(1)—C(2) C(3)—C(4) <i>s</i>	C(7)—C(8) C(8)—C(9) <i>s</i>
<i>E</i> (143 K)	1.378 (5)	1.435 (7)	1.409 (7)	1.399 (7)
<i>A</i> (173 K)	1.352 (4)	1.393 (3)	1.425 (3)	1.467 (3)
<i>B</i> (295 K)	1.516 (12)	1.373 (7)	1.493 (8)	1.479 (7)
<i>C</i> (ca 295 K, molecule 1)	1.341 (5)	1.406 (4)	1.456 (4)	1.489 (3)
Reference bonds	Double (simple) 1.337 (6)	Aromatic 1.395 (3)	Graphite 1.4210 (1)	Single (partial) 1.476
	Single (partial) 1.507			

Thiophene rings

Compound	C(10)—C(11) C(5)—C(6) <i>d</i>	C(9)—C(10) C(6)—C(7) <i>s</i>
<i>E</i> (143 K)	1.344 (8)	1.452 (7)
<i>A</i> (173 K)	1.345 (4)	1.426 (4)
<i>B</i> (295 K)	1.340 (8)	1.430 (8)
	S(1)—C(1) S(2)—C(4) <i>s</i>	S(1)—C(11) S(2)—C(5) <i>s</i>
<i>E</i> (143 K)	1.729 (5)	1.723 (5)
<i>A</i> (173 K)	1.738 (3)	1.716 (3)
<i>B</i> (295 K)	1.722 (6)	1.714 (7)

* See deposition footnote.

such interactions have been minimized by taking a boat form.

Thus, there is a gradual change in the detailed geometry throughout the molecules of the series in the crystalline state. This change in geometry parallels that of chemical properties.

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G II

X-ray Crystallographic Studies on Cycloheptadithiophene Compounds and Similar Systems.

XI. The Structure of 9*H*-Cyclohepta[2,1-*b*:4,5-*b'*]dithiophen-4-ylum Perchlorate at 173 K

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Abstract

$C_{11}H_7S_2^+ \cdot ClO_4^-$ is monoclinic, space group $P2_1/c$, with $a = 10.4615$ (18), $b = 25.7202$ (26), $c = 26.8840$ (23) Å, $\beta = 94.657$ (10)° at 173 K, and $Z = 24$. The structure was refined to an R of 0.12 for 3794 non-zero counter reflexions at 173 K. The cations are approximately planar. Aromatic character is indicated by the relatively uniform C—C lengths. The S—C bonds are equal. The structure is built up of columns of cations with the anions in between. There is orientational disorder, and diffuse scattering is observed in Weissenberg photographs. A comparison with another phase of the same compound and a similar compound is made.

Introduction

The title compound is composed of cycloheptadithiophenylum cations and ClO_4^- anions ($G \cdot ClO_4^-$, Fig. 1); it has two modifications. Aurivillius (1974) determined the crystal structure of the phase with a small unit cell (phase I, G I) and found the cation to be approximately planar. The present crystal structure is that of another phase with a large unit cell (phase II, G II). The structure of a corresponding compound, 4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-ylum tetrafluoroborate (*E*), has been determined and its molecular structure related to a series of similar compounds (Andersson, 1979). The cation *G* has an even higher degree of aromaticity than *E* (Yom-Tov, 1972).

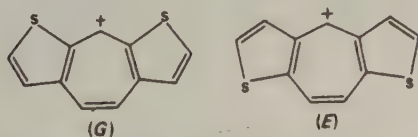


Fig. 1. Schematic drawings of molecules *G* (9*H*-cyclohepta[2,1-*b*:4,5-*b'*]dithiophen-4-ylum perchlorate), and *E* (4*H*-cyclohepta[1,2-*b*:5,4-*b'*]dithiophen-4-ylum tetrafluoroborate).

The packing of the present compound has been studied, and compared between the two phases and the corresponding compound mentioned above. The structure was determined at 173 K.

Experimental

Crystals were formed when a saturated solution of $G \cdot ClO_4^-$ in boiling acetonitrile was cooled to room temperature. By cooling air, plate-like crystals (phase I) were formed, and by using ice-water needles (phase II) were obtained.

It was possible to transform phase II to phase I by heating to 458 K for some days, or by shaking the crystals in their saturated solution at room temperature, but not the reverse. When a single crystal of II was transformed to I, it retained its habit, but the extinction observed with polarized light did not persist. It was concluded that II is metastable at the temperatures used.

Table 1. Crystal data (*G* II)

$C_{11}H_7S_2^+ \cdot ClO_4^-$, $M_r = 302.8$, monoclinic, space group $P2_1/c$, $Z = 24$, $D_m = 1.7$, $D_x = 1.66$ Mg m⁻³

	173 K	295 K
<i>a</i>	10.4615 (18) Å	10.5565 (8) Å
<i>b</i>	25.7202 (26)	25.7669 (11)
<i>c</i>	26.8840 (23)	26.8556 (10)
β	94.657 (10)°	94.465 (6)°
<i>V</i>	7210 (3) Å ³	7283 (3) Å ³
μ (Mo $K\alpha$)	0.66 mm ⁻¹	
λ (Mo $K\alpha_1$)	0.70930 Å	
λ (Cu $K\alpha_1$)		1.54051 Å

JAN-ERIK ANDERSSON

Table 2. *Positional parameters ($\times 10^4$) and isotropic thermal parameters with e.s.d.'s in parentheses (173 K, G II)*The expression for the isotropic temperature factor is $\exp [-8\pi^2 U(\sin \theta/\lambda)^2]$.

	<i>x</i>	<i>y</i>	<i>z</i>	$8\pi^2 U$ ($\text{\AA}^2$)		<i>x</i>	<i>y</i>	<i>z</i>	$8\pi^2 U$ ($\text{\AA}^2$)
S(1)A	5906 (8)	5598 (3)	-278 (3)		C(1)B	6067 (29)	5029 (11)	2680 (11)	2.2 (6)
S(2)A	6419 (8)	6490 (3)	1525 (3)		C(2)B	6063 (29)	5563 (11)	2564 (11)	2.2 (6)
S(1)B	6138 (8)	4101 (3)	3084 (3)		C(3)B	6253 (34)	5980 (13)	2921 (12)	3.4 (7)
S(2)B	6582 (9)	5698 (4)	4373 (3)		C(4)B	6368 (32)	5968 (12)	3431 (12)	3.2 (7)
S(1)C	504 (8)	6520 (3)	6951 (3)		C(5)B	6539 (33)	6436 (13)	3723 (12)	3.5 (7)
S(2)C	53 (9)	4887 (3)	5716 (3)		C(6)B	6602 (32)	6345 (13)	4200 (12)	3.3 (7)
S(1)D	1670 (8)	2278 (3)	5950 (3)		C(7)B	6440 (29)	5519 (11)	3758 (11)	2.4 (6)
S(2)D	676 (7)	2037 (3)	3977 (3)		C(8)B	6358 (28)	4982 (11)	3651 (10)	2.3 (6)
S(1)E	7465 (8)	2740 (3)	3733 (3)		C(9)B	6209 (27)	4774 (10)	3160 (10)	1.6 (5)
S(2)E	8282 (8)	2777 (3)	5727 (3)		C(10)B	5888 (31)	4147 (12)	2430 (11)	2.6 (7)
S(1)F	2658 (8)	1008 (3)	7603 (3)		C(11)B	5963 (27)	4656 (10)	2273 (10)	1.6 (6)
S(2)F	2776 (9)	-1068 (3)	7809 (3)		C(1)C	585 (27)	5603 (10)	7387 (10)	1.7 (6)
ClA	3675 (8)	8934 (3)	320 (3)	3.3 (2)	C(2)C	569 (29)	5078 (12)	7507 (11)	2.4 (6)
ClB	7788 (7)	4829 (3)	1078 (3)	1.9 (1)	C(3)C	453 (29)	4672 (11)	7187 (11)	2.2 (6)
ClC	2861 (8)	5211 (3)	1430 (3)	2.5 (2)	C(4)C	345 (25)	4657 (10)	6661 (9)	1.2 (5)
ClD	5337 (8)	2652 (3)	2110 (3)	3.2 (2)	C(5)C	218 (29)	4168 (11)	6397 (11)	2.3 (6)
ClE	1016 (7)	3462 (3)	4662 (3)	1.9 (1)	C(6)C	90 (30)	4241 (12)	5911 (11)	2.7 (6)
ClF	658 (8)	2893 (3)	7374 (3)	2.6 (2)	C(7)C	309 (24)	5090 (9)	6336 (9)	0.9 (5)
O(1)A	2370 (34)	8877 (14)	-46 (12)	11.6 (9)	C(8)C	317 (30)	5610 (11)	6416 (11)	2.5 (6)
O(2)A	3334 (34)	8822 (14)	762 (13)	13.8 (9)	C(9)C	498 (25)	5833 (10)	6904 (9)	0.9 (5)
O(3)A	4122 (23)	9449 (9)	247 (8)	4.0 (5)	C(10)C	769 (30)	6493 (12)	7601 (11)	2.4 (6)
O(4)A	4311 (34)	8572 (14)	76 (13)	12.2 (9)	C(11)C	824 (30)	6008 (12)	7786 (11)	2.6 (6)
O(1)B	7123 (21)	4366 (8)	1220 (8)	3.4 (5)	C(1)D	1124 (25)	1322 (10)	5659 (9)	1.4 (5)
O(2)B	7449 (26)	4914 (10)	545 (10)	5.6 (6)	C(2)D	804 (26)	863 (10)	5389 (10)	1.5 (6)
O(3)B	7367 (21)	5274 (8)	1351 (8)	3.1 (5)	C(3)D	559 (28)	806 (11)	4880 (10)	2.1 (6)
O(4)B	9160 (21)	4772 (8)	1181 (8)	3.4 (5)	C(4)D	559 (29)	1187 (11)	4493 (11)	2.4 (6)
O(1)C	2155 (23)	5180 (9)	947 (8)	4.0 (5)	C(5)D	198 (27)	1026 (10)	3990 (10)	1.8 (6)
O(2)C	2140 (25)	5558 (10)	1734 (9)	5.2 (6)	C(6)D	267 (32)	1463 (12)	3666 (12)	2.9 (7)
O(3)C	3008 (22)	4699 (8)	1649 (8)	3.6 (5)	C(7)D	849 (24)	1737 (9)	4566 (9)	0.8 (5)
O(4)C	4113 (30)	5411 (12)	1374 (11)	7.3 (7)	C(8)D	1089 (26)	2031 (10)	4971 (10)	1.7 (6)
O(1)D	4555 (35)	2979 (14)	2311 (13)	13.6 (9)	C(9)D	1252 (28)	1834 (11)	5484 (10)	2.1 (6)
O(2)D	5186 (22)	2134 (9)	2304 (8)	3.7 (5)	C(10)D	1736 (32)	1791 (13)	6407 (12)	3.2 (7)
O(3)D	4854 (36)	2584 (13)	1565 (13)	11.5 (9)	C(11)D	1375 (30)	1302 (12)	6213 (11)	2.7 (6)
O(4)D	6682 (30)	2799 (11)	2163 (11)	7.1 (7)	C(1)E	7377 (0)	1842 (0)	4157 (0)	1.7 (0)
O(1)E	2202 (22)	3223 (8)	4621 (8)	4.0 (5)	C(2)E	7294 (0)	1418 (0)	4508 (0)	2.9 (0)
O(2)E	470 (18)	3274 (7)	5110 (7)	2.4 (4)	C(3)E	7606 (0)	1405 (0)	5037 (0)	2.0 (0)
O(3)E	212 (19)	3316 (7)	4240 (7)	2.7 (4)	C(4)E	7801 (0)	1829 (0)	5348 (0)	2.6 (0)
O(4)E	1149 (22)	4009 (9)	4686 (8)	3.9 (5)	C(5)E	7967 (0)	1809 (0)	5886 (0)	1.9 (0)
O(1)F	-271 (36)	2761 (14)	7718 (13)	9.6 (9)	C(6)E	8229 (30)	2251 (12)	6119 (11)	2.7 (6)
O(2)F	-40 (30)	2872 (12)	6925 (11)	7.0 (7)	C(7)E	7958 (29)	2390 (11)	5193 (11)	2.3 (6)
O(3)F	1144 (23)	3400 (9)	7502 (8)	4.3 (5)	C(8)E	7827 (28)	2627 (11)	4735 (10)	1.9 (6)
O(4)F	1575 (30)	2507 (11)	7445 (11)	7.3 (7)	C(9)E	7584 (25)	2375 (9)	4270 (9)	0.9 (5)
C(1)A	5500 (28)	6596 (11)	-273 (11)	2.3 (6)	C(10)E	7117 (33)	2233 (13)	3361 (12)	3.4 (7)
C(2)A	5385 (31)	7119 (12)	-146 (11)	2.7 (7)	C(11)E	7070 (0)	1754 (0)	3622 (0)	2.6 (0)
C(3)A	5569 (32)	7385 (13)	312 (12)	3.5 (7)	C(1)F	2971 (24)	681 (9)	8529 (9)	0.7 (5)
C(4)A	5810 (27)	7127 (11)	795 (10)	2.0 (6)	C(2)F	3253 (31)	377 (12)	8982 (11)	2.5 (6)
C(5)A	5892 (28)	7423 (11)	1235 (10)	2.1 (6)	C(3)F	3313 (28)	-151 (11)	9024 (10)	1.9 (6)
C(6)A	6302 (36)	7131 (14)	1675 (13)	4.2 (8)	C(4)F	3107 (28)	-543 (11)	8650 (11)	1.8 (6)
C(7)A	6081 (28)	6581 (11)	902 (10)	2.1 (6)	C(5)F	3224 (32)	-1077 (13)	8774 (12)	3.2 (7)
C(8)A	6052 (29)	6159 (11)	563 (11)	2.4 (6)	C(6)F	3051 (32)	-1396 (12)	8374 (12)	3.0 (7)
C(9)A	5850 (27)	6180 (11)	42 (10)	1.8 (6)	C(7)F	2943 (26)	-467 (10)	8141 (10)	1.5 (5)
C(10)A	5513 (32)	5928 (13)	-826 (12)	3.2 (7)	C(8)F	2838 (29)	-14 (11)	7831 (11)	2.2 (6)
C(11)A	5377 (29)	6446 (12)	-770 (11)	2.2 (6)	C(9)F	2874 (28)	491 (11)	8026 (10)	2.0 (6)
					C(10)F	2694 (29)	1457 (11)	8089 (11)	2.2 (6)
					C(11)F	2888 (27)	1228 (10)	8543 (10)	2.3 (6)

CYCLOHEPTADITHIOPHENE COMPOUNDS AND SIMILAR SYSTEMS. XI

X-ray diffraction work

A single crystal (part of a needle), with a volume of $6 \times 10^{-3} \text{ mm}^3$, was used. Cell dimensions and intensities were determined on a four-circle diffractometer (Enraf-Nonius CAD-4) with equatorial geometry and graphite-monochromatized Mo K radiation ($\lambda = 0.71073 \text{ \AA}$). The temperature was kept at 173 K by a flow of cold nitrogen gas (Danielsson, Grenthe & Oskarsson, 1976). Some crystal data are given in Table 1. The intensities of 7410 reflexions, of which 3794 had $I > 3\sigma_c(I)$, were measured. Further details of the measurements are similar to those in Andersson (1978).*

Determination and refinement of the structure

The intensities were corrected for Lorentz and polarization effects but not for absorption ($\mu = 0.66 \text{ mm}^{-1}$). Systematic extinctions at 173 K were $h0l$ with $l = 2n + 1$ and $0k0$ with $k = 2n + 1$. Weak intensities were found for some $h0l$ reflexions with l odd, but could be discarded.* Thus, space group $P2_1/c$ was considered.

The structure was solved by symbolic addition (MULTAN, Germain, Main & Woolfson, 1971). Subsequent electron-density syntheses and least-squares refinements gave the positions of all atoms except H. In some ClO_4^- groups the O positions were uncertain due to disorder.

In the final full-matrix refinement, the function minimized was $\sum w(\Delta|F|)^2$, where $\Delta|F| = |F_o| - |F_c|$. The weight function was $w^{-1} = \sigma_c^2(|F_o|) + 0.000625|F_o|^2 + 0.10$. Scattering factors were those of Doyle & Turner (1968). All atoms were not refined simultaneously, and H atoms could not be refined. Some of the ClO_4^- groups were disordered, and probably additional orientations were possible but were not accounted for. Anisotropic temperature factors were refined for the S atoms,* but not for the Cl atoms.

The final $R = \sum |\Delta|F|| / \sum |F_o| = 0.122$ and $R_w = [\sum w(\Delta|F|)^2 / \sum w|F_o|^2]^{1/2} = 0.164$. The goodness of fit $S = [\sum w(\Delta|F|)^2 / (m - n)]^{1/2} = 1.01$, where m is the number of observations and n the number of parameters. The final coordinates are given in Table 2.* The maximum residual electron density was $1.65 \text{ e \AA}^{-3}$. The thermal parameters of some ClO_4^- groups were large, indicating disorder. For some reflexions $\Delta|F|/\sigma(\Delta|F|)$ values were very large.* Weissenberg photographs showed diffuse intensities indicating disorder.

* See deposition footnote.

Discussion of the structure at 173 K (G II)

The present structure has six independent units, consisting of a cycloheptadithiophenylum cation (G in Fig. 1) and a ClO_4^- ion, in the unit cell. It is built up of columns of cations along a with ClO_4^- ions in between (Fig. 2a). A view of one asymmetric unit is shown in Fig. 2(b). The best planes of the cations have approximately the same direction. The cations of column C , F , B are approximately in the direction of a ; D , A , E are somewhat more tilted. The cation A in column D , A , E deviates slightly, being tilted relative to D and E (Table 3), and correspondingly F relative to C and B . The greatest angle between planes is $A-D$, $161.6(5)^\circ$. Within a column the distance between the planes is approximately $a/3 = 3.487 \text{ \AA}$.

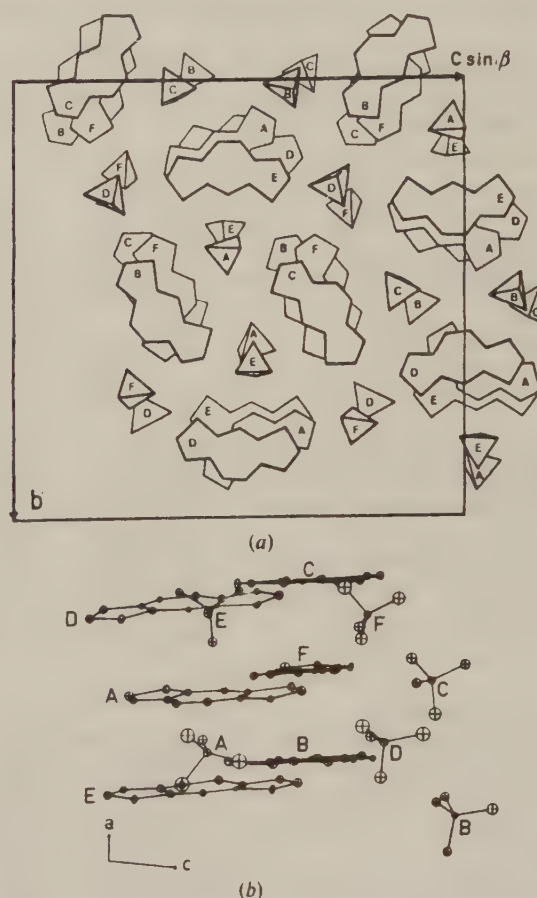


Fig. 2. Projections of (a) G II in the direction of a (H omitted), and (b) the asymmetric unit of G II in the direction of b (H omitted).

* Additional experimental details, anisotropic thermal parameters, lists of structure factors, additional least-squares planes, angles in cations, and distances and angles in ClO_4^- have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35694 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

JAN-ERIK ANDERSSON

Table 3. Angles ($^{\circ}$) between the best planes of the cations (G II)

Within column		Between columns	
<i>D-A</i>	161.6 (5)	<i>D-C</i>	170.8 (6)
<i>A-E</i>	163.6 (6)	<i>-F</i>	168.6 (8)
<i>E-D</i>	177.5 (7)	<i>-B</i>	171.0 (6)
<i>C-F</i>	176.5 (20)	<i>A-C</i>	169.4 (5)
<i>F-B</i>	175.6 (21)	<i>-F</i>	172.7 (13)
<i>B-C</i>	179.1 (5)	<i>-B</i>	168.6 (5)

The shortest contacts between the cations are given in Table 4. Most of these contacts are within the columns. Of the ClO_4^- ions, *A*, *D* and *F* seem to be disordered, having high temperature factors for the O atoms. Short distances between ClO_4^- ions are within the columns. Between the columns, the distances are, in general, considerably longer. The distances between cations and anions are short relative to the van der Waals distances and the distances between ions of the same charge.

Of the disordered ClO_4^- ions, *D* has no and *F* only one short contact to cations, in contrast to *B*, *C* and *E* which have at least two short contacts to different O atoms. ClO_4^- ion *A*, which is also disordered, has two short contacts, but to the same O atom. The short contacts to a cation are preferably to the S atoms. There are not short contacts to all cations.

Table 4. Intermolecular distances ($\text{\AA}$) at 173 K (GII)

Van der Waals radii (Bondi, 1964) and upper limits are given. These are followed by the atoms and the distances between them at 173 K. Distances between columns are marked with an asterisk. For notation see Fig. 4b.

Distances between cations

VdW 3.5	<3.82	<i>S(1)F-C(10)B</i>	3.47 (4)
<i>S(2)A-S(2)D</i>	3.70 (2)	<i>-C(1)C</i>	3.55 (3)
<i>S(1)B-S(1)F</i>	3.77 (2)	<i>-C(9)C</i>	3.68 (3)
<i>S(1)C-S(1)E*</i>	3.49 (2)	<i>-C(11)C</i>	3.71 (4)
<i>S(1)D-S(2)E</i>	3.77 (2)	<i>S(2)F-C(3)B</i>	3.63 (4)
VdW 3.45	<3.74	VdW 3.4	<3.5
<i>S(1)A-C(2)D</i>	3.55 (4)	<i>C(1)A-C(3)E</i>	3.40 (4)
<i>S(2)A-C(6)D</i>	3.55 (4)	<i>-C(4)E</i>	3.49 (4)
<i>S(1)B-C(9)C</i>	3.52 (3)	<i>C(2)A-C(4)E</i>	3.42 (4)
<i>-C(9)F</i>	3.56 (4)	<i>C(4)A-C(1)E</i>	3.43 (4)
<i>-C(1)F</i>	3.66 (4)	<i>C(5)A-C(10)E</i>	3.45 (5)
<i>S(2)B-C(6)C</i>	3.63 (4)	<i>C(1)B-C(8)F</i>	3.44 (5)
<i>S(1)C-C(10)F</i>	3.34 (4)	<i>C(4)B-C(5)F</i>	3.50 (5)
<i>S(1)D-C(6)E</i>	3.67 (4)	<i>C(7)B-C(4)F</i>	3.48 (5)
<i>S(2)D-C(9)E</i>	3.50 (3)	<i>C(8)B-C(3)F</i>	3.44 (5)
<i>-C(1)E</i>	3.56 (1)	<i>-C(7)C</i>	3.49 (4)
<i>-C(4)A</i>	3.69 (4)	<i>C(8)C-C(1)F</i>	3.46 (4)
<i>S(1)E-C(5)A</i>	3.61 (4)	<i>C(4)D-C(2)E</i>	3.47 (3)
<i>S(2)E-C(6)F*</i>	3.59 (4)	<i>C(6)D-C(11)E</i>	3.42 (4)
<i>-C(5)F*</i>	3.65 (4)		

Distances between anions

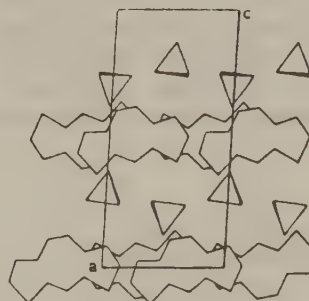
VdW 3.0	<3.87	VdW 3.3	<3.40
<i>O(1)A-O(2)E</i>	3.34 (5)	<i>O(2)A-S(1)B</i>	3.19 (4)
<i>O(4)A-O(1)E</i>	3.78 (5)	<i>-S(1)E</i>	3.24 (4)
<i>O(3)B-O(4)C</i>	3.43 (4)	<i>O(2)B-S(1)A</i>	3.17 (4)
<i>O(4)B-O(1)C</i>	3.41 (4)	<i>O(3)B-S(2)A</i>	3.33 (3)
<i>O(1)D-O(4)F</i>	3.41 (6)	<i>O(2)C-S(2)F</i>	3.19 (3)
<i>O(4)D-O(1)F</i>	3.70 (5)	<i>O(3)C-S(1)F</i>	3.19 (3)
<i>O(3)A-O(3)A*</i>	3.69 (5)	<i>O(2)E-S(2)E</i>	3.20 (3)
		VdW 3.2	<3.24
		<i>O(1)B-C(10)A</i>	2.97 (4)
		<i>O(1)E-C(3)A</i>	3.17 (4)
		<i>O(2)F-C(6)E</i>	3.15 (5)

Comparison with phase I (G I)

This phase, with a small unit cell and only one independent unit, was determined at 295 K by Aurivillius (1974). It has a significantly smaller volume per molecule, $300.3 (4) \text{\AA}^3$, compared to that of phase II at room temperature, $303.4 (2) \text{\AA}^3$ (Tables 1,5). Here there are layers of cations with layers of ClO_4^- in between (Fig. 3). Within a layer the cations are parallel and the distance between the best planes is $3.443 \text{\AA}$.

Table 5. Crystal data (G I and E)

	$\text{C}_{11}\text{H}_7\text{S}_2^+ \cdot \text{ClO}_4^-$, G I, monoclinic, $P2_1/n$	$\text{C}_{11}\text{H}_7\text{S}_2^+ \cdot \text{BF}_4^-$, E, triclinic, $P\bar{1}$
<i>a</i>	6.819 (2) $\text{\AA}$	7.1949 (12) $\text{\AA}$
<i>b</i>	12.032 (4)	8.7203 (12)
<i>c</i>	14.677 (6)	9.5967 (20)
α		105.787 (15) $^{\circ}$
β	93.60 (3) $^{\circ}$	99.074 (13)
γ		96.817 (13)
<i>V</i>	1201 (1) $\text{\AA}^3$	536.8 (6) $\text{\AA}^3$
<i>Z</i>	4	2
<i>T</i>	295 K	143 K

Fig. 3. A view of G I with *b* towards the reader (H omitted).

CYCLOHEPTADITHIOPHENE COMPOUNDS AND SIMILAR SYSTEMS. XI

Short contacts between cations are within the layers (Table 6, Fig. 4a). As phases I and II are studied at different temperatures it is not possible to make a direct comparison of short distances. ClO_4^- is disordered and is represented by two orientations. The shortest distance between anions, 3.7 Å, is between the anion layers.

The ClO_4^- ion has several short contacts to cations from its two orientations, preferably to the S atoms and C(9).

Table 6. Intermolecular distances (Å) at 295 K (*G* I)

Van der Waals radii (Bondi, 1964) and upper limits are given. These are followed by the atoms and the distances between them. Distances between layers are marked with an asterisk (cf. Fig. 4a).

Distances between cations		Distances between anions	
VdW 3.5	<4.0	VdW 3.0	<4.0
S(1)—S(8)	3.716 (4)	O(1)—O(1)*	3.709 (24)
VdW 3.45	<3.77	Distances between different ions	
S(1)—C(7)	3.563 (12)	VdW 3.3	<3.42
—C(3)	3.696 (11)	O(4)—S(8)	3.028 (25)
S(8)—C(6)	3.745 (12)	—S(1)	3.190 (25)
VdW 3.4	<3.53	O(5)—S(1)	3.275 (33)
C(6)—C(VII)	3.521 (15)	VdW 3.2	<3.24
C(7)—C(VI)	3.426 (16)	O(2)—C(9)	3.081 (33)
C(2)—C(VI)	3.497 (16)	O(3)—C(9)	3.094 (23)
C(2)—C(2)	3.503 (25)	O(6)—C(9)	3.106 (62)
		O(7)—C(4)	3.058 (43)

Comparison with *E*

This ion (Fig. 1) is similar to *G*. The volume per unit is smaller than for *G* I and *G* II, 281.9 (3) Å³ at 173 K (Table 5). The parallel cations form layers with the anions in between (Fig. 5). Within a layer the distance between the cations is 3.347 Å.

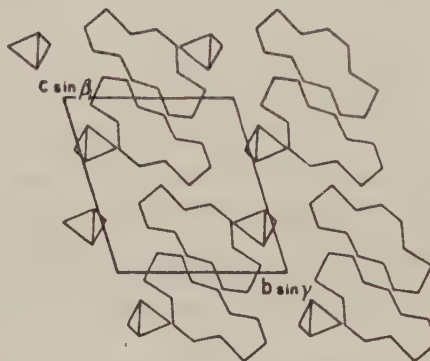


Fig. 5. A view of *E* with *a* towards the reader (*H* omitted).

Most of the short contacts between cations are within a layer. The BF_4^- ion is disordered (two orientations) with the shortest contacts within the layers.

The distances from the BF_4^- ion to the cations are short and mainly to the S atoms.

Conformation

From a statistical point of view (Table 7, Fig. 4b) each of the cations except *F* is planar and only ring (III) in *F* is non-planar.* The angle between planes (I) and (II) is significant for *E* and the mean of the angles between planes (I) and (II) is 178 (2)°.

Bond distances (Fig. 6) and angles* indicate that the e.s.d.'s are correctly estimated and that systematic deviations occur between the left and right sides of *A*, *B*, *C*, and *E* (Hamilton, 1974). The mean values are given in Fig. 7(a). The S—C bonds are equal. In the central ring the C—C lengths are about the same, and in the thiophene rings differ more. Some angles differ from

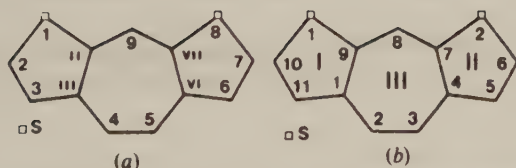


Fig. 4. Schematic diagrams (a) of the cycloheptadithiophenyl cation in *G* I showing the numbering of the atoms (cf. Table 6), and (b) defining the numbering of atoms and planes for molecules *A* to *F* in *G* II (cf. Table 4). In the following diagrams the molecules are oriented in the same way.

* See deposition footnote.

JAN-ERIK ANDERSSON

Table 7. Least-squares planes (*G* II)

Deviations ($\text{\AA} \times 10^3$) of the atoms from the best planes of the molecules, and angles ($^\circ$) between planes (I) and (II) are given. Weights proportional to the atomic numbers are used. The e.s.d.'s for the deviations of S and C are 8 and 32 ($\text{\AA} \times 10^3$) respectively (cf. Fig. 4b).

	<i>X</i> = <i>A</i>	<i>X</i> = <i>B</i>	<i>X</i> = <i>C</i>	<i>X</i> = <i>D</i>	<i>X</i> = <i>E</i>	<i>X</i> = <i>F</i>
S(1 <i>X</i>)	7	22	33	13	-3	-41
S(2 <i>X</i>)	2	-24	4	-11	6	47
C(1 <i>X</i>)	-34	-20	26	11	44	37
C(2 <i>X</i>)	-14	-39	47	6	-38	-49
C(3 <i>X</i>)	55	20	40	-9	70	-63
C(4 <i>X</i>)	-29	-4	-15	-23	-5	20
C(5 <i>X</i>)	-45	50	1	36	-48	-17
C(6 <i>X</i>)	52	-12	-14	6	-27	16
C(7 <i>X</i>)	-10	19	-52	-42	26	-24
C(8 <i>X</i>)	-36	12	-1	35	-3	-72
C(9 <i>X</i>)	17	14	-21	24	26	-59
C(10 <i>X</i>)	-6	-57	-40	-54	-32	97
C(11 <i>X</i>)	24	21	-70	6	-22	97

Planes	<i>A</i>	<i>B</i>	<i>C</i>
(I)-(II)	178.6 (12)	178.1 (14)	178.7 (13)
	<i>D</i>	<i>E</i>	<i>F</i>
(I)-(II)	179.1 (10)	176.9 (8)	174.8 (27)

the ideal values for five- and seven-membered rings. H atoms were not determined. The e.s.d.'s of the ClO_4^- ions are underestimated for *A*, *D* and *F* and the mean Cl—O distance is 1.43 (4) $\text{\AA}$.*

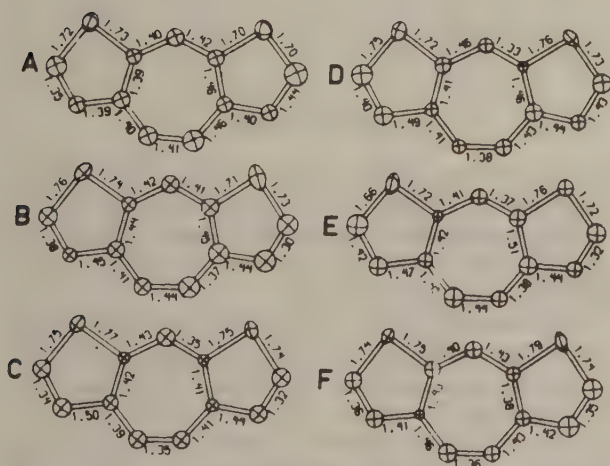


Fig. 6. The cycloheptadithiophenyl cations *G* II at 173 K. Distances ($\text{\AA}$) for non-hydrogen atoms are presented. The e.s.d.'s are for C—S 0.033 and for C—C 0.045 $\text{\AA}$. The numbering of the atoms and the ring system is as in Fig. 4(b) and 50% probability ellipsoids are shown.

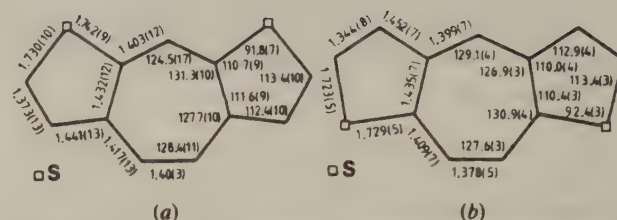


Fig. 7. Mean values of bond distances ($\text{\AA}$) and angles ($^\circ$) for (a) the cycloheptadithiophenyl cations *G* II at 173 K (the numbering of the atoms is as in Fig. 4b), and (b) the cycloheptadithiophenyl cation *E* at 143 K.

Comparison with *G* I

The structure *G* I was determined at 295 K, in contrast to the present structure *G* II, and with one exception the bond lengths in the cation are shorter, probably due to thermal motion. The angles agree. The conformations in *G* I and *G* II are similar. Each separate ring is planar but not the molecule as a whole. The angle I—II is 177.7 (4) $^\circ$.

Comparison with *E*

E is determined at 143 K, and the cation has a boat conformation with 175.3 (4) $^\circ$ between planes (I) and (II). The average distances and angles are given in Fig. 7(b). Comparable distances agree well with the distances of *G* II, although the differences between the shortest and longest distances in the seven- and five-membered rings are larger for *E* than for *G* II. This is in accordance with a lower degree of aromaticity for *E* than for *G*.

In the seven-membered ring the top angle is larger. In both *E* and *G* the angle nearest the S atom is the largest.

* See deposition footnote.

CYCLOHEPTADITHIOPHENE COMPOUNDS AND SIMILAR SYSTEMS. XI

Disorder

Areas with diffuse intensity appear in Weissenberg photographs around **b** and **c** at 295 and 173 K (Cu K) on every third bow near and across *h* ($h = 3, 6, 9; -6 \leq l \leq 4; |k| \leq 3$) and at 204. This is also where the strongest reflexions are situated and they have diffuse intensity at their sides. Around **a** the disorder is observed as streaks in $3kl$ at low θ values. The diffuse bows have their centers of intensity on **a** and thus represent the direction of **a** while 204 gives another direction. As there are three cations, with their planes perpendicular to **a** and separated by $a/3$ in the columns along **a**, but only two ClO_4^- ions, it is assumed that the diffuse rows are caused by some disorder of the cations and the diffuse area at 204 by the ClO_4^- ions.

The normals to the cation planes point approximately in the direction of **a**, which is the direction the diffuse intensity represents. This might be an indication of orientational disorder, and another indication comes from the location of the residual electron density. There are peaks, mainly at the midpoints of bonds, which fit well with a rotated molecule, although this is not the only explanation. Thus, a fraction of the cations are probably rotated by 180° . There are high peaks near the ClO_4^- ions **A**, **D** and **F**, which also have high temperature factors for the O atoms, indicating a high degree of orientational disorder.

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